JARA-FIT

Jülich Aachen Research Alliance for
Fundamentals of Future Information Technology

Annual Report 2013

Forschungszentrum Jülich
RWTH Aachen
Dear Reader

You hold the VIth edition of the JARA-FIT Annual Report in your hands. As every year, the core of this booklet is formed by the two-page scientific reports that illustrate the successful work that JARA scientists have carried out and published in 2013. Although large in number, these reports are only a small selection of what has been achieved. We hope that you will find them an interesting read.

For us in JARA-FIT, the year 2013 was dominated by the preparation of the third POF review that took place in early 2014. The POF process (POF stands for Programme-oriented Funding) is the 5-yearly strategic evaluation in the Helmholtz Association. It is carried out in accordance with the Helmholtz Mission “to contribute to solving grand challenges which face society, science and industry by performing top-rate research in strategic programmes in the fields of Aeronautics, Space and Transport, Earth and Environment, Energy, Health, Key Technologies as well as the Structure of Matter”.

For the Jülich members of JARA-FIT the funding for the years 2015 to 2019 was at stake. After intensive deliberations, we had decided to build on our successful Fundamentals of Information Technology programme and develop it further, albeit with a stronger emphasis on energy efficient (“green”) information technology. Furthermore, the new programme, entitled “Future Information Technology – Fundamentals, Novel Concepts, and Energy Efficiency” now includes contributions from the Helmholtz Zentrum Berlin as well as Forschungszentrum Jülich.

JARA-FIT played an important role in the design of the new programme and its evaluation. From the Jülich perspective it was heartening to see the strong support from our Aachen colleagues, just as researchers of Forschungszentrum Jülich had supported their colleagues in the Aachen bid in the last round of the Excellence Initiative. This mutual support shows that JARA is really alive, sustained by the insight that in the field of information technology research neither of the two sides can prosper without the other. Although the final report has not been released yet, the evaluators did convey their appreciation of our programme clearly. Apart from scientific excellence it was also the partnership in JARA-FIT which impressed the referees.

With the POF evaluation behind us, we will continue our research on future information technology, spanning a broad range of work in, e.g., silicon, spintronics, topological matter, phase change materials, resistive switching devices, molecular electronics, quantum information and strongly correlated systems. Nobody knows where this journey will take us, because the field of information technology, that is “the application of computers and telecommunications equipment to store, retrieve, transmit and manipulate data” (Wikipedia), is still full of surprises, even 55 years after the term information technology in its modern sense first appeared in a 1958 article by Harold J. Leavitt and Thomas L. Whisler in the Harvard Business Review.

This article, entitled “Management in 1980’s” is an interesting document. Leavitt and Whisler write: “Over the last decade a new technology has begun to take hold in American business, one so new that its significance is still difficult to evaluate ... The new technology does not yet have a single established name. We shall call it information technology (IT). It is composed of several related parts. One includes techniques for processing large amounts of information rapidly, and it is epitomized by the high-speed computer. A second part centers around the application of statistical and mathematical methods to decision-making problems; it is represented by techniques like mathematical programing, and by methodologies like operations research. A third part is in the offing, though its applications have not yet emerged very clearly; it consists of the simulation of higher-order thinking through computer programs.”

What follows is an analysis how this new technology will, in the authors’ projection, change how businesses are run (“Information technology is likely to have its greatest impact on middle and top management”). While they do make some realistic predictions, from today’s perspective we would say that they probably still underestimated the impact of IT on business, let alone on society as a whole.

However, future generations will most likely also find our visions of the future of IT somehow limited. But precisely this is what makes working in this field so exciting: It offers the opportunity to witness and shape the emergence of something really new, with surprises looming around every corner. We at JARA-FIT are grateful that we can be part of this endeavour.

Stefan Tautz
Scientific Director JARA-FIT

Matthias Wuttig
Scientific Director JARA-FIT
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JARA-FIT Highlights

JARA-FIT scientist Rainer Waser received the Gottfried Wilhelm Leibniz Award of the German Research Foundation

On December 5, 2013, the Joint Committee of the German Research Foundation, DFG for short, has announced the prize winners in the Gottfried Wilhelm Leibniz program. Among these, JARA-FIT scientist Rainer Waser, Professor of Materials in Electrical Engineering at RWTH Aachen University and director of the Institute of Electronic Materials at Forschungszentrum Jülich. He receives 2.5 million euros for his research activities in the next seven years. The DFG has emphasized that “Rainer Waser is an outstanding researcher in both the natural sciences and engineering. His research is unusually broad, ranging from pure solid-state chemistry and defect chemistry to electronic properties and modelling, the technology of new materials and the physics of electronic oxide devices. With a high-calibre global network, Waser is one of the most cited representatives of his field and is highly respected as a lecturer and mentor for early career researchers.” The prize is awarded in recognition of his research for the use of resistive switches as memories in information technology. Initial efforts were made in this field by other researchers from the 1960s onwards, but failed to achieve scientific breakthroughs or technological prospects. Rainer Waser discovered, in 2006, the basic mechanism as a nanionic redox process controlling the switching characteristic. This opened up new possibilities in the miniaturisation of memory components and offers enormous potential for energy-saving, as resistive memories use up to two orders of magnitude less energy than their conventional counterparts.

JARA-FIT director Matthias Wuttig received ERC Advanced Grant from the European Research Council

Matthias Wuttig, JARA-FIT director and spokesperson for the Collaborative Research Centre 917 “Nanoswitches”, has been awarded an Advanced Grant from the European Research Council, ERC. The grants are intended to support the very best research to be conducted in EU member states and associated countries. They are to allow exceptional, established leaders in research to pursue ground-breaking high-risk projects that open new directions in their respective research fields and blur the boundary between basic and applied research. Matthias Wuttig receives funding worth 2.1 Mio. € over a period of five years for his project "Tuning Disorder in Chalcogenides to realize Advanced Functional Devices". Recently, he demonstrated an Anderson-type transition from insulating to metallic behaviour in phase change materials upon annealing. However, to fully utilize these ideas it is mandatory to realize devices with a more directly controllable degree of disorder. Within the framework of his project, he wants to develop a tuneable Anderson insulator to delocalize charge carriers. This should allow him to address a) the transition from an insulator to a metal, the impact of disorder on superconductors (b) and topological insulators (c) and, finally, d) the ability to control thermolectric properties by tunable electronic disorder. From the results to be obtained he expects consequences for a wide range of materials listed in a "treasure map", with promising new technological applications in various devices.
Aachen Materials Research Institute DWI becomes member of the Leibniz Association

Research at DWI in Aachen is concerned with the development of materials that are themselves active or can interact with a specific environment. This interdisciplinary research concept brings together expert researchers from the fields of polymer science, biotechnology, physics and process engineering. In its 2013 summer meeting the German Council of Science and Humanities (Wissenschaftsrat) recommended to accept the DWI as a member of the Leibniz Association. The Joint Science Conference (GWK) and the members of the Leibniz Association ratified this recommendation. The DWI joined the Leibniz Association in January 2014 while changing its name to: “DWI – Leibniz Institute for Interactive Materials”. (Six RWTH professors from the core scientific board of DWI.) The institute is co-directed by Alexander Böker, a member of JARA-FIT. His research focusses on the synthesis of functional nanoparticles and their guided self-assembly to form functional superstructures. Within the framework of JARA-FIT, his research deals with electric field directed self-assembly of block copolymer/metal nanoparticle composites to generate new pathways for the lithography-free miniaturization of future consumer electronics.

Hatsujiro Hashimoto Medal for Chunlin Jia

Chunlin Jia of the Ernst Ruska-Centre received the 2014 Hatsujiro Hashimoto Medal from the International Federation of Societies for Microscopy. The award, honouring the outstanding contributions of individual scientists in the application of microscopy and other related techniques in physics and material sciences, is named after the pioneer of microscopy research, Hatsujiro Hashimoto. Chunlin Jia will be presented with the prize in September 2014 at the 18th International Microscopy Congress in Prague.

Microsystem Engineering Conference in Aachen

Between October 14th and 16th, 2013, about 900 attendees participated in the Microsystem Engineering Conference, taking place at the Aachen Eurogress Conference Center. The event was jointly organized by the RWTH Institute of Materials in Electrical Engineering, headed by JARA-FIT member Wilfried Mokwa, the Federal Ministry of Education and Research, and the Association for Electrical, Electronic & Information Technologies, VDE for short. Today, there is a multitude of products relying on micro electronics, power electronics, and micro systems engineering. Recent years saw a trend from the realisation of mere components to the development of intelligent networked systems, such as “smart systems”, which are likely to contribute to the solution of many of the pressing problems of the 21st century. The focus of the conference was on electronic systems in the service of energy supply, energy efficiency, and production automation.
Dedication of Helmholtz Nanoelectronic Facility

On 27th September 2013 NRW Science Minister Svenja Schulze dedicated together with Karl-Eugen Hutmacher, chairman of the supervisory board of the Forschungszentrum Jülich, and Achim Bachem, chairman of the board of directors, the Helmholtz Nanoelectronic Facility (HNF) and handed it to future users. Subsequently, 800 visitors used the opportunity to visit the HNF in guided group tours.

From left to right: Sebastian Schmidt (Member of the Board of Directors for Scientific Division I), Achim Bachem (Chairman of the Board of Directors), Karl-Eugen Hutmacher (Chairman of Supervisory Board), NRW Science Minister Svenja Schulze, Andreas Offenhauser, and Detlev Grützmacher (Directors of HNF).

Detlev Grützmacher explained the „Nanocluster“, an epitaxy cluster for the combination and creation of new electronic materials. With this ceremony the first part of operating license for the HNF was granted. For the managing director of the HNF, Wolfgang Albrecht, this meant that the conditions were met to finish the hook-up and start the ramp-up of the systems and processes in the coming months.

The ceremony finished a period of intensive efforts:

**Placing equipment**

**Construction phase**

End of 2013, the trainings of the operational staff and the Facility Management department started, followed by the safety trainings of the first users. In April 2014, the full operation license for HNF was granted.
DFG establishes Research Training Group on "Quantum Many-Body Methods in Condensed Matter Systems" at RWTH Aachen University

The German Research Foundation (Deutsche Forschungsgemeinschaft; DFG) provides 3.6 million Euro funding for a new Research Training Group on "Quantum Many-Body Methods in Condensed Matter Systems" at RWTH Aachen University. This was decided by the Grants Committee at its spring session 2014. The Research Training Group will offer doctoral researchers the opportunity to complete their theses in a structured research and qualification program at outstanding academic level. Setting up this program was possible by combining the complementary expertise of researchers from RWTH and the Forschungszentrum Jülich within the JARA framework. The Research topic is a fundamental problem of theoretical condensed matter physics, namely obtaining a better understanding of the collective quantum phenomena, such as magnetism and superconductivity emerging from the interplay of the large number of constituents of a solid. The goal is to provide a description of interacting many-body systems that is as realistic and accurate as possible. Potential applications of the results range from functional materials to nanoelectronics. Spokesperson is JARA-FIT member Volker Meden.

New Management of JARA-FIT

Stefan Tautz (Peter Grünberg Institute, Forschungszentrum Jülich) has become Managing Director of JARA-FIT, beginning 1. January 2014.

JARA-FIT scientist Janine Splettstößer received Wallenberg Academy Fellowship

Janine Splettstößer has been awarded a Wallenberg Academy Fellowship. She receives about 1.3 million Euros for her research projects over the next five years. The Swedish Knut and Alice Wallenberg Foundation is a funding institution to support research in Sweden. Splettstößer was nominated for the fellowship by Chalmers University of Technology, Gothenburg, where she started her research activities in January 2014. Since October 2009, she was head of a team of early-career researchers at RWTH Aachen University interested in the theory of time-dependent control of single electrons in nanoelectronic systems. She continues her collaborations with JARA-FIT after leaving RWTH Aachen University, for instance, as an associate of the Research Training Group on "Quantum Many-Body Methods in Condensed Matter Systems".

We congratulate...

...the former JARA-FIT associates Sabine Andergassen and Dirk Schuricht on their new positions. Until January 2012 Sabine Andergassen was a junior professor at the Institute for Theory of Statistical Physics of RWTH and JARA-FIT member. She then took on an assistant professorship at Vienna University and now accepted a call for a chair at the Institut for Theoretical Physics at Tübingen University. Professor Andergassen starts her new position in fall 2014 and continues her research on electronic correlations in mesoscopic systems. From 2010 until September 2013 Dirk Schuricht was an Emmy-Noether Scholar at the Institute for Theory of Statistical Physics at RWTH where he pursued his research on nonequilibrium physics of low-dimensional quantum many-body systems. He accepted the offer for an assistant professorship at Utrecht University which he took on in October 2013.

JARA-FIT Lab Course Nanoelectronics

This year, 40 students participated in our one week 9th JARA-FIT Lab Course Nanoelectronics. Addressees were master students of physics, electrical engineering, chemistry, and materials science. The idea of the Nanoelectronics lab course is to bring students as early as possible into contact with real top-level research equipment used by Jülich JARA-FIT scientists. The Lab Course also introduced the students to current research topics of JARA-FIT. The students received introductory lectures, performed one experiment per day in small groups, and were able to discuss scientific issues as well as carrier issues with their JARA-FIT supervisors. The students came from Aachen as part of their master courses, additionally 15 students came from all over Germany.
45th IFF Spring School: "Computing Solids: Models, ab-initio methods and supercomputing" with Record Demand for Places

From the 10th March to 21st March 2014, Jülich hosted the IFF Spring School for the 45th time in its long history. The annual intensive course was organized this time by the Peter Grünberg Institute-1 and Institute for Advanced Simulation-1 together with the Theoretical Solid State Physics Group from the RWTH Aachen University. Under the scientific direction of JARA-FIT members Stefan Blügel and Volker Meden together with Nicole Helbig and Daniel Wortmann the Spring School was devoted to the computing of solids with bringing together models, ab-initio methods and supercomputing. 63 women and 216 men from Germany and abroad participated in the Spring School. There were almost twice as many applications from students and young scientists for places on the two-week compact course – more than ever before.

The IFF Spring School 2014 provided a comprehensive introduction to modern concepts, theories and methods enabling the theoretical description of many-electron systems. The hallmark of the school was in the concept of discussing density functional theory type ab-initio approaches as well as specialized many-body techniques for strongly correlated systems emphasizing the new opportunities provided by high-performance computers with advanced architectures. The school linked these three aspects to the study of emergent properties of solids and non-equilibrium quantum transport. The guiding principle for the selection of the specialized subjects was their timeliness and the expertise of the scientific institutes involved. The school started with introductory lectures on the many-electron problem. Basic lectures introduced the different methodologies but will also bring in cutting edge research in the field. The formulation of realistic model Hamiltonians linked density functional theory to the many-body methods. The school moved on to discuss solutions to the many-body problem of model systems, either analytically using renormalization group techniques, or numerically using different computational implementations. The School advanced to the calculation of different materials and physical effects. One emphasis was the quantum and topological transport properties. The School also included lectures on computational topics addressing the recent and future advances in computer architecture and technology. These lectures put special focus on how the computational resources can be exploited for the simulation of complex materials, for example, via parallel programming or how large computing resources change the paradigm of materials research.

Autumn School on Correlated Electrons: Emergent Phenomena in Correlated Matter

Emergent phenomena are the hallmark of many-body systems, and yet to unravel their nature remains one of the central challenges in condensed-matter physics. In order to advance our understanding it is crucial to learn from the different manifestations of emergence as well as from the interplay of different emergent phases, such as magnetism and superconductivity. For addressing such problems, it is necessary to master a broad spectrum of techniques from traditionally separate branches of research, ranging from ab-initio approaches based on density-functional theory to advanced many-body methods to electron-lattice coupling and dynamics. The Autumn School on Correlated Electrons: Emergent Phenomena in Correlated Matter was held in the week of 23th to 27th September 2013 in Jülich aiming to analyze emergence in some of its major manifestations in the solid-state and compare methodologies used to address specific aspects. The scope of the school was to introduce advanced graduate students and up to the essence of emergence and the modern approaches for modeling emergent properties of correlated matter. The school was led by Eva Pavarini, Institute for Advanced Simulation (IAS), and Erik Koch, German
Research School for Simulation Sciences (GRS), together with Ulrich Schollwöck from LMU München. More than 100 young researchers were interested in the Autumn-School. The school also gave the students the opportunity to present their own projects and to expand their network in the global research community represented by participants from 20 countries, besides Germany and countries within the EU, including the USA, Canada, India, Brazil, Turkey, Egypt, Algeria, and even Sudan, Ethiopia and Nigeria. Ten of the international participants received Travel Awards from the Institute for Complex Adaptive Matter (ICAM). ICAM also sponsored three overseas speakers, while many of the European speakers were supported by the DFG Research Unit 1346 “Dynamical Mean-Field Approach with Predictive Power for Strongly Correlated Materials”. Comprehensive lecture notes were collected in a book which has been made available via Open Access.

Institute of Neuroscience and Medicine and Institute for Advanced Simulation at Forschungszentrum Jülich get involved in the EU-Flagship “Human Brain Project”

The goal of the European Future & Emerging Technologies (FET) Flagship Project “Human Brain Project” (HBP) is to build a completely new Information Communication Technology (ICT) infrastructure for future neuroscience, future medicine and future computing that will catalyse a global collaborative effort to understand the human brain and its diseases and ultimately to emulate its computational capabilities. Jülich is one of the major consortium partners. The Jülich Supercomputing Centre and the Institute of Neuroscience and Medicine at Forschungszentrum Jülich have leading roles. JARA-FIT member Sonja Grün heads the work package “Tools for the analysis of functional data” where statistical tools are defined, selected and developed that make it possible to analyze and compare multi-scale data from brain dynamics from experiments and from brain simulation. Markus Diesmann is leader of the task “The network simulator – from point neurons to box models”. The software NEST (Neural Simulation Technology, www.nest-initiative.org) developed at the institute is the central simulation engine of the HBP on the level of neurons and synapses. Abigail Morrison develops “Models of biologically realistic network states during wakefulness and sleep”.

Frontiers of Knowledge Award for Pioneers of Electron Microscopy

Maximilian Haider from CEOS GmbH in Heidelberg, Harald Rose, Senior Professor at the University of Ulm, and JARA-Seniorprofessor Knut Urban are the recipients of the 2014 Banco Bilbao Vizcaya Argentaria Foundations Frontiers of Knowledge Award in the Basic Sciences category. The BBVA Foundation decided to award the prize to the three scientists in recognition of the central role they played in developing a new generation of aberration-corrected electron microscopes. These microscopes made it possible to image atomic structures right down to displacements on the picometre scale, which revolutionised materials science.

The three physicists joined forces in the early 1990s with the aim of correcting the image aberrations in electron-optical lenses that have existed since the invention of electron microscopy. They developed a corrector that compensates for these aberrations in a manner similar to the divergent lens in an optical microscope and they produced a prototype aberration-corrected electron microscope in 1997. The most important element in the corrector, which Maximilian Haider constructed based on a design proposed by Harald Rose, is the superimposed magnetic multipoles and, later, electrostatic multipoles. However, the microscopic images produced in this way cannot be directly interpreted. They do not show the atomic structures directly and they are strongly influenced by the laws of quantum physics. It was Knut Urban and his colleagues at the Ernst Ruska-Centre, a joint undertaking of the Forschungszentrum Jülich and RWTH Aachen University, who made insights into the atomic world a reality by applying their own complex computer-assisted quantum-physics techniques of image calculation and interpretation.

PICO 2013 Second Conference on Frontiers of Aberration Corrected Electron Microscopy

PICO 2013 – the second conference on frontiers of aberration corrected electron microscopy which was organised by the Jülich Branch of the Ernst Ruska-Centre together with the Triebenberg Laboratory of the Technical University of Dresden – was held in Kasteel Vaalsbroek from 9th to 12th October 2013. Second in a
series of biennial conferences, PICO 2013 focused on the most recent advances and future directions in methods and applications of aberration corrected electron microscopy for the study of structural and electronic properties of the solid state. The meeting attracted about 140 participants including company representatives and a good number of international colleagues from 19 countries. Topical issues of aberration corrected microscopy were highlighted in 33 keynote presentations given by leading invited speakers. About the same numbers of contributions were scheduled for poster presentations. Conference proceedings were published in a special issue of Ultramicroscopy (Volume 134, 2013). A follow-up conference, PICO 2015, is scheduled to take place again in Kasteel Vaalsbroek and will be held from 19th to 23rd April 2015.
General Information
JARA-FIT Members

Prof. Dr. St. Appelt, Lehrstuhl für Technische und Makromolekulare Chemie, Lehr- und Forschungsgebiet Niederfeld-NMR (Methoden der NMR), RWTH Aachen
Zentralinstitut für Elektronik, Forschungszentrum Jülich

Prof. Dr. H. Bluhm, II. Physikalisches Institut C, RWTH Aachen

Prof. Dr. S. Blügel, Peter Grünberg Institut – Quanten-Theorie der Materialien, Forschungszentrum Jülich
Institute for Advanced Simulation, Forschungszentrum Jülich

Prof. Dr. T. Brückel, Peter Grünberg Institut – Streumethoden, Forschungszentrum Jülich
Jülich Centre for Neutron Science, Forschungszentrum Jülich

Prof. Dr. A. Böker, Makromolekulare Materialien und Oberflächen, DWI – Leibniz Institute for Interactive Materials, Aachen

Prof. Dr. D. P. DiVincenzo, Institut für Quanteninformation, RWTH Aachen
Peter Grünberg Institut – Theoretische Nanoelektronik, Forschungszentrum Jülich
Institute for Advanced Simulation, Forschungszentrum Jülich

Prof. Dr. R. Dronskowski, Lehrstuhl für Festkörper- und Quantenchemie und Institut für Anorganische Chemie, RWTH Aachen

Prof. Dr. R. Dunin-Borkowski, Peter Grünberg Institut – Mikrostrukturforschung, Forschungszentrum Jülich
Ernst Ruska-Centre für Mikroskopie und Spektroskopie mit Elektronen

Prof. Dr. D. Grützmacher, Peter Grünberg Institut – Halbleiter-Nanoelektronik, Forschungszentrum Jülich

Prof. Dr. S. Grün, Institut für Neurowissenschaften und Medizin, Computational and Systems Neuroscience
Forschungszentrum Jülich

Prof. Dr. C. Honerkamp, Institut für Theoretische Festkörperphysik, RWTH Aachen

Prof. Dr. L. Juschkin, Lehr- und Forschungsgebiet Experimentalphysik des Extrem-Ultravioletts, RWTH Aachen

Prof. Dr. P. Kögerler, Institut für Anorganische Chemie (Molekularer Magnetismus), RWTH Aachen
Peter Grünberg Institut – Elektronische Eigenschaften, Forschungszentrum Jülich

Prof. Dr. U. Klemradt, II. Physikalisches Institut B, RWTH Aachen

Prof. Dr. J. Knoch, Institut für Halbleitertechnik, RWTH Aachen

Prof. Dr. P. Loosen, Lehrstuhl für Technologie Optischer Systeme, RWTH Aachen
Fraunhofer-Institut für Lasertechnik, Aachen

Prof. Dr. S. Mantl, Peter Grünberg Institut – Halbleiter-Nanoelektronik, Forschungszentrum Jülich

Prof. Dr. M. Martin, Institut für Physikalische Chemie, RWTH Aachen

Prof. Dr. J. Mayer, Gemeinschaftslabor für Elektronenmikroskopie, RWTH Aachen
Ernst Ruska-Centre für Mikroskopie und Spektroskopie mit Elektronen

Prof. Dr. R. Mazzarello, Institut für Theoretische Festkörperphysik, RWTH Aachen

Prof. Dr. V. Meden, Institut für Theorie der Statistischen Physik, RWTH Aachen

Prof. Dr. Chr. Melcher, Lehrstuhl I für Mathematik, RWTH Aachen

Prof. Dr. W. Mokwa, Institut für Werkstoffe der Elektrotechnik 1 – Mikrostrukturintegration, RWTH Aachen

Prof. Dr. M. Morgenstern, II. Physikalisches Institut B, RWTH Aachen

Prof. Dr. T. Noll, Lehrstuhl für Allgemeine Elektrotechnik und Datenverarbeitungssysteme, RWTH Aachen
Prof. Dr. A. Offenhäusser, Peter Grünberg Institut – Bioelektronik, Forschungszentrum Jülich
Institute of Complex Systems, Forschungszentrum Jülich

Prof. Dr. E. Pavarini, Peter Grünberg Institut & Institut for Advanced Simulation, Forschungszentrum Jülich

Prof. Dr. R. Poprawe Fraunhofer-Institut für Lasertechnik, Aachen

Prof. Dr. G. Roth, Institut für Kristallographie, RWTH Aachen

Prof. Dr. H. Schoeller, Institut für Theorie der Statistischen Physik, RWTH Aachen

Prof. Dr. U. Simon, Institut für Anorganische Chemie, RWTH Aachen

Prof. Dr. C. Stampfer, II. Physikalisches Institut A, RWTH Aachen
Peter Grünberg Institut – Halbleiter-Nanoelektronik, Forschungszentrum Jülich

Prof. Dr. C. M. Schneider, Peter Grünberg Institut – Elektronische Eigenschaften, Forschungszentrum Jülich

Prof. Dr. T. Taubner, I. Physikalisches Institut A, RWTH Aachen

Prof. Dr. S. Tautz, Peter Grünberg Institut – Funktionale Nanostrukturen an Oberflächen, Forschungszentrum Jülich

Prof. Dr. B.M. Terhal, Institut für Quanteninformation, RWTH Aachen

Prof. Dr. A. Vescan, Lehr- und Forschungsgebiet GaN-Bauelementtechnologie, RWTH Aachen

Prof. Dr. R. Waser, Institut für Werkstoffe der Elektrotechnik 2, RWTH Aachen
Peter Grünberg Institut – Elektronische Materialien, Forschungszentrum Jülich

Prof. Dr. M. Wegewijs, Peter Grünberg Institut – Theoretische Nanoelektronik, Forschungszentrum Jülich

Prof. Dr. S. Wessel, Institut für Theoretische Festkörperphysik, RWTH Aachen

Prof. Dr. J. Witzens, Lehr- und Forschungsgebiet Integrierte Photonik, RWTH Aachen

Prof. Dr. M. Wuttig, I. Physikalisches Institut A, RWTH Aachen
**JARA-FIT Institutes**

**Systeme der Elektronik (ZEA-2), Forschungszentrum Jülich &
Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen**

St. Appelt

Our research revolves around spin order generation, the manipulation, measurement and transfer of spin order by combining Hyperpolarization technology with Nuclear Magnetic Resonance (NMR) spectroscopy. Starting from states with high spin orders, like nuclear singlet states or highly premagnetized (hyperpolarized) spin systems, we investigate the field dependency of the complexity, and thus information content, of corresponding NMR spectra in very low magnetic fields. Our research includes chemical synthesis as a means for substrate generation and optimization of spin order transfer, the development and construction of new hardware for mobile NMR spectroscopy as well as the investigation of the underlying quantum mechanical principles of coupled NMR spectroscopy in low magnetic fields.

**Peter Grünberg Institut / Institute for Advanced Simulation – Quantum Theory of Materials, Forschungszentrum Jülich**

S. Blügel

The analysis and computation of electronic properties of solid-state systems relevant for basic science and practical applications in collaboration with experimentalists are the hallmark of our research. An important asset of our institute is the competence in developing conceptual and computational methods (density functional theory, many-body perturbation theory and beyond, topology). Emphasis is on the investigation of complex magnetism, magnetism in reduced dimensions, oxide interfaces and heterostructures, oxides with large defects, topological insulators, graphene, organic molecules in contact with metallic and insulating substrates, spin- and spin-orbit-dependent electronic transport phenomena, collective excitations and quasi-particles, and high-performance computing. A second research theme is nano-scale tribology, friction, adhesion, plastic deformation. Computational materials science research is established by combining first-principles results with macroscopic methods (molecular dynamics, Monte Carlo).

**II. Physikalisches Institut (IIC), RWTH Aachen**

H. Bluhm

The research group is aiming to realize highly coherent two-level quantum systems in semiconductor quantum dots for quantum information processing. The group studies the physics governing these devices and pushes forward their technological development. Key topics include high fidelity control, decoherence measurements and multi-qubit circuits. In addition, the group is pursuing scanning SQUID microscopy at ultra-low temperatures for magnetic imaging and ultra-sensitive magnetic measurements on mesoscopic structures.

**Lehrstuhl für Makromolekulare Materialien und Oberflächen (Physikalische Chemie) & DWI – Leibniz Institute for Interactive Materials**

A. Böker

The chair of Macromolecular Materials and Surfaces is part of the DWI – Leibniz Institute for Interactive Materials. The DWI is associated with RWTH Aachen University via a cooperation agreement focusing on polymer / soft matter materials development with the mission of novel and active properties. Under the heading “Science for Innovation” we aim at a tailor-made surface functionality of soft materials, especially fibers, films, membranes, textiles, and biomaterials. Beyond knowledge-oriented, basic approaches, work at DWI is dedicated to the translation and implementation of this knowledge into application-oriented concepts for functional films and surfaces, antimicrobial polymers and surfaces, encapsulation and release, functional membranes, and biomedical devices. The major research topics at the chair of Macromolecular Materials and Surfaces include bioconjugate polymer materials, nanoparticle composites and guided self-assembly.
At the Institute of Scattering Methods, we focus on the investigation of structural and magnetic order, fluctuations and excitations in complex or nanostructured magnetic systems and highly correlated electron systems. Our research is directed at obtaining a microscopic atomic understanding based on fundamental interaction mechanisms. The aim is to relate this microscopic information to macroscopic physical properties. To achieve this ambitious goal, we employ the most advanced synchrotron X-ray and neutron scattering methods and place great emphasis on the complementary use of these two probes. Some of our efforts are devoted to dedicated sample preparation and characterization from thin films and multilayers via nano-patterned structures to single crystals for a wide range of materials from metals to oxides.

The behavior of interacting electrons in nano-scale structures is a primarily focus. The Kondo effect, involving the interaction of an isolated spin impurity with conduction electrons, or the formation and transport of high-spin complexes forming spin quadrupoles, are particular areas of expertise. Novel computational techniques permit accurate calculations with thousands of atoms, and in complex multi-functional perovskites. Correlated electrons also form the basis of the physical creation of qubits, and the coherence and dynamics of such qubits, and multiqubit systems, is being investigated.

The institute has a broad agenda of topics in the theory of quantum information. New principles for the implementation of quantum computation in noisy systems, particularly Fermionic many-body systems. This includes particularly the investigation of Majorana qubits realized in semiconductor nanowires. Protocols for fault tolerance in quantum computation are investigated. New applications of the theory of quantum entanglement for efficient classical simulations are developed. Detailed modeling of hardware for superconducting qubits and circuit-quantum electrodynamic structures is underway, in close collaboration with experiment.

The institute is specialized in the fields of synthetic and quantum-theoretical solid-state chemistry, bordering with materials science, solid-state and theoretical physics, crystallography, as well as quantum and computational chemistry. In detail, we synthesize novel, sometimes extremely sensitive, compounds and elucidate their compositions and crystal structures by means of X-ray and neutron diffractional techniques. The characterization of their physical properties, that is electronic transport and magnetism, also plays a very important role.

The institute works on topical fields in solid-state physics. Strategically two directions are followed: firstly, to make key contributions to the development and application of ultra-high resolution transmission electron microscopy, in particular to aberration-corrected electron optics for subangstrom structural and spectroscopic resolution, and secondly, to produce a number of selected material systems and to study their physical properties. Examples are high-temperature superconductors and the novel complex metallic
alloys. The former provides the basis of our work on SQUID sensors and on ac-Josephson effect based Hilbert spectroscopy for the THz range. The head of the institute is co-director of the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons.

**Institute of Neuroscience and Medicine - Computational and Systems Neuroscience & Institute for Advanced Simulations - Theoretical Neuroscience, Forschungszentrum Jülich**

S. Grün together with M. Diesmann and A. Morrison

Progress in the understanding of complex systems like the brain can only be achieved by integrating models on many different scales. The Institute of Neuroscience and Medicine, Computational and Systems Neuroscience, analyses massively-parallel electrophysiological data in their relation to behavior, maintains a network of experimental partner laboratories, and develops corresponding statistical tools. On this basis the INM-6 develops multi-scale models of the brain, combining data-driven development of brain theory with the bottom-up approach of directly simulated structured networks, and the top down approach, mapping functional models of higher brain function to spiking dynamics. Moreover, theoretical descriptions from the microscopic level of single cells and synapses to effective equations capturing interacting brain areas are built. Substantial resources are devoted to the development of the required simulation technology. Close collaborations with partner laboratories in neuromorphic computing ensure that novel algorithms rapidly enter those devices and neurobiologically realistic benchmarks are evaluated.

**Peter Grünberg Institut – Halbleiter-Nanoelektronik, Forschungszentrum Jülich**

D. Grützmacher

The institute’s research activities are based on its competence in semiconductor heterostructure and nanostructure research, both in fundamental and device physics as well as in material and process development. They address three major fields. (1) Si-CMOS technology: novel materials and new device concepts are used to drive CMOS to its limits. (2) III-V and III-nitride semiconductors: high frequency devices are developed up to and into the terahertz range. (3) Nanostructures for quantum electronics: devices based on the tunneling effect and ferromagnetic/semiconductor hybrid structures are investigated, the latter particularly in view of spintronic applications.

**Institut für Theoretische Festkörperphysik, RWTH Aachen**

C. Honerkamp, R. Mazzarello, M. Schmidt, S. Wessel

The research groups in this institute study many-particle interactions in solids, ranging from quantum effects in magnetic systems over electron correlation effects leading to unconventional superconductivity and magnetism to the dynamics of structural phase transitions. Recent work has focused on interaction effects in graphene systems, topological insulators, pnictide high-temperature superconductors and chalcogenide phase-change materials. The powerful theoretical methods employed and developed here comprise quantum Monte Carlo techniques, the functional renormalization group, density-functional theory and molecular dynamics.

**Lehr- und Forschungsgebiet Experimentalphysik des Extrem-Ultravioletts, RWTH Aachen**

L. Juschkin

The research in the field of extreme ultraviolet (EUV) radiation is a major contribution for nanoelectronics and future developments in information technology. At the Chair for Experimental Physics of EUV different aspects related to the EUV radiation are investigated ranging from generation and characterization of EUV, to wave propagation and light-matter interaction as well as developing new methods and applications. In combination of EUV interference lithography and the self-organized growth of nanostructures novel materials are prepared, and their properties are analyzed. Moreover, in cooperation with the Fraunhofer Institute for Laser Technology in Aachen different concepts of EUV sources are investigated. On the application side, a series of measurement procedures for which the specific features of EUV radiation can be used, for example, the EUV microscopy and spectroscopic reflectometry, are investigated.
II. Physikalisches Institut (IIB) – Röntgenstreuung und Phasenumwandlungen, RWTH Aachen
U. Klemradt

Our research is centered at the investigation of nanoscale structures and fluctuations, with focus on nanoparticles, polymer-based nanocomposites and ferroic materials. Of particular interest are phase transitions in smart materials like shape memory alloys. The main experimental tools are X-ray scattering and acoustic emission spectroscopy. We use both laboratory tubes and synchrotron facilities for X-ray experiments and operate a 6-circle diffractometer at HASYLAB (DESY, Hamburg), which is especially suited to the analysis of thin films. Core techniques are small angle X-ray scattering (SAXS), grazing incidence scattering (GISAXS and reflectometry), and photon correlation spectroscopy using coherent X-rays (XPCS).

Institut für Halbleitertechnik, RWTH Aachen
J. Knoch

The institute carries out research on semiconductor technology and device with a special focus on low power and energy harvesting technologies with the long-term vision of energy autonomous systems. To be specific, we work on nanoelectronics transistor devices based on Si- and III-V nanowires as well as on carbon nanotubes and graphene particularly aiming at a realization of so-called steep slope switches that enable a significant reduction of the power consumption of highly integrated circuits. In addition, the institute has broad experience in the science and engineering of Si wafer-based solar cells and also performs research on Si-based third generation photovoltaic cells. A combination of our know-how in micro- and nanotechnology with the solar cell technology is used to investigate and realize novel concepts for energy harvesting and storage based e.g. on efficient direct solar water splitting.

Institut für Anorganische Chemie – Molekularer Magnetismus, RWTH Aachen & Peter Grünberg Institut – Elektronische Eigenschaften (Molekularer Magnetismus), Forschungszentrum Jülich
P. Kögerler

The Molecular Magnetism Group focuses on the chemistry and fundamental physics of discrete and networked magnetically functionalized inorganic molecules. Based on its experience with the control and understanding of magnetic characteristics of purely molecular origin, the group synthesizes magnetic materials based on transition metal clusters that exhibit a complex interplay of charge transport and static/dynamic magnetic properties such as phase transitions, hysteresis, or quantum tunneling. To functionally combine magnetic state switching and charge transport in systems for FIT spintronic devices, the molecule-surface interface is addressed, in particular employing surface structure-directed coupling reactions to molecular aggregates, single-stranded molecular conductors, or 2D networks.

Lehrstuhl für Technologie Optischer Systeme, RWTH Aachen (RWTH-TOS) & Fraunhofer-Institut für Lasertechnik, Aachen
P. Loosen

Extreme ultraviolet radiation (XUV, 1-50 nm, or EUV at 13.5 nm) enables new optical, analytical and manufacturing technologies because of its characteristic interaction with matter, its short wavelength and recent progress on light sources and optical components (e.g. EUV lithography). XUV tools are already deployed by the semiconductor industry, which significantly pushes the further development of XUV technology. Future applications which will support scientific progress in a variety of fields such as nanoelectronics or biotechnology are also within the scope of our research. Activities include structuring on a nanometer scale using interference lithography, XUV microscopy for imaging of dynamic processes or at-wavelength inspection of multilayer mask-blanks for hidden defects, and characterization of thin film coated surfaces using grazing-incidence reflectometry.

Institut für Physikalische Chemie (IPC), RWTH Aachen
M. Martin

The institute’s research activities are based on its competence in the physical chemistry of solids with a special emphasis on defects and diffusion in inorganic solids, in particular oxides. Within JARA-FIT two major fields are addressed. (1) Ionic transport: transport of oxygen ions in the bulk, across and along grain
boundaries and in space charge zones is investigated by means of secondary ion mass spectrometry (SIMS), density functional theory and Monte Carlo simulations. (2) Electronic transport: amorphous and highly non-stoichiometric oxides are investigated concerning correlations between structure, electrical conductivity, and electronic structure with a view to applications in resistive switching.

**GFE – Gemeinschaftslabor für Elektronenmikroskopie & Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons**

**J. Mayer**

GFE is a central facility of RWTH Aachen University and has state-of-the-art equipment in the fields of transmission electron microscopy, scanning electron microscopy, electron microprobe analysis, focused ion beam instruments and atomic force microscopy. GFE provides services for a large number of institutes from RWTH Aachen University and a broad range of industrial companies. In the field of information technology, GFE participates in research projects on nonvolatile memories and on nanoscale CMOS devices. The head of the GFE is co-director of the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and coordinates the RWTH user activities and contribution to the Centre.

**Institut für Theorie der Statistischen Physik, RWTH Aachen**

**V. Meden, H. Schoeller, M. Wegewijs**

The members of the institute are investigating the spectral and transport properties of low-dimensional quantum systems in contact with heat and particle reservoirs. The research focuses on the development of many-body methods for strongly correlated mesoscopic systems in nonequilibrium (quantum field theory and renormalization group in nonequilibrium) as well as on the application to experimentally realizable physical systems like semiconductor quantum dots, quantum wires (e.g. carbon nanotubes), and molecular systems.

**Lehrstuhl I für Mathematik, RWTH Aachen**

**Ch. Melcher**

The research at our institute has a focus on nonlinear partial differential equations from mathematical physics and materials science. We are particularly interested in the emergence and dynamics of patterns and topological solitons in models from micromagnetics and Ginzburg-Landau theory. Using tools from functional and multiscale analysis, our aim is to capture the qualitative behavior of solutions to such complex theories and, if possible, to identify simpler models, whose behavior is easier to understand or simulate.

**Institute of Materials in Electrical Engineering I, RWTH Aachen**

**W. Mokwa**

The institute’s research activities are focused on the development of micro systems for medical and life science applications. Main activities lie on coupling of biological systems to technical systems, development of "intelligent" implants and prostheses and micro fluidic systems for biotechnology and medical diagnostics. For the development of these systems silicon and thin film technologies, silicon micromechanics, micro electroplating, soft lithography as well as sophisticated packaging technologies are used in a clean room of about 600 m².

**II. Physikalisches Institut (IIB) – Rastersondenmethoden, RWTH Aachen**

**M. Morgenstern**

The research group develops scanning probe methods working in particular at low temperatures down to 0.3 K and in high magnetic fields up to 14 T in order to investigate the electronic structure of interacting electron systems and systems relevant for nano electronic applications. Thereby, we exploit the advantage of mapping the electronic structure down to the atomic scale at an energy resolution down to 0.1 meV, but also use the scanning probes for the excitation of the systems under study. Current topics of interest are graphene flakes and monolayers, quantum Hall physics in III-V-materials, confined wave functions in quantum dots, artificial spin chains, nanomagnetic systems, and phase change materials.
Chair of Electrical Engineering and Computer Systems, RWTH Aachen

T. Noll

The research group is working on developing semiconductor-based architectural strategies for high-throughput digital signal processing, circuit concepts, and design methodologies, with a focus on energy-efficient circuits. The group wants to contribute to the development of highly-integrated, massively-parallel architectures based on nano-electronic device concepts. Emphasis is placed on the issue of reliability and fault-tolerant design.

Peter Grünberg Institut / Institute of Complex Systems – Bioelektronik, Forschungszentrum Jülich

A. Offenhäusser

Our research aims for the application of micro- and nanoelectronics to brain and life sciences. Research activities focus on two main topics: electromagnetic sensing and bioelectronic hybrid systems. This requires a better understanding of the interactions between biological systems and electronic substrates and the development of new technologies, resulting in new concepts of the interconnection of biological matter to electronic probes, and novel approaches to study cellular functions at the micro- and nanoscale. Here, we aim at a better understanding of the physiological behavior and mechanisms of neuronal information processing and new tools for diagnostics and imaging.

Institute of Crystallography, RWTH Aachen

G. Roth

The institute’s research profile covers the topics synthesis, structure and properties of novel materials. The synthetic activities include the preparation of new or crystal-chemically modified compounds with interesting properties in bulk poly- or single-crystalline form. Crystal and magnetic structures are studied by powder and single crystal X-ray as well as neutron diffraction methods (outstation at FRM-II/Garching) with special emphasis on complex, defect dominated systems such as partially disordered, incommensurately modulated structures and composite crystals. Among the materials recently studied are superconductors (modulated CaAlSi), fullerenes (C70 high pressure polymer), spin-chain-compounds (vanadates and cuprates) and pyroxene-type multiferroics.

II. Physikalisches Institut (IIA), RWTH Aachen

C. Stampfer

Our research activities are focused on (i) carbon-based quantum electronics, (ii) semiconductor-based spin-electronics, and on (iii) topological insulators. For instance, we focus on studying electronic and mechanical properties of carbon and Bi2Se3-based systems that have critical dimensions on the nanometer scale. Such structures approach the atomic scale and the ultimate limit of solid state miniaturization. In particular we investigate systems based on nanostructured graphene (a monoatomic sheet of graphite) and carbon nanotubes. Current interests include (i) developing advanced processing technologies for fabricating novel nanodevices, (ii) understanding new and interesting transport phenomena that arise in these devices, and (iii) learning how to control and detect the charge, spin and mechanical degrees of freedom in these systems. Potential applications include ultra-fast electronics, new spin-based nanoelectronic device concepts and applied quantum technology.

Peter Grünberg Institut – Elektronische Eigenschaften, Forschungszentrum Jülich

C. M. Schneider

The institute is engaged in the study of electronic and magnetic phenomena in novel materials and is one of the birthplaces of magnetoelectronics. Present research concentrates on the fundamental aspects, properties, and control of spin-transfer processes. The activities cover several facets, e.g., the development of new magnetic materials or the engineering of interfaces to improve the spin injection efficiency. Further important research fields comprise nanomagnetism and nanospintronics, which may form a bridge to quantum information processing. To this end new techniques and procedures are being established. Spintronics is also firmly linked to the condensed matter program, providing access to and knowledge about new material classes for use in the spintronics activities of the present program.
Institut für Anorganische Chemie (IAC), RWTH Aachen

U. Simon

Our research is devoted to functional metal and metal oxide nanostructures. One focus is the wet chemical tailoring and the characterization of ligand stabilized metal nanoparticles of different geometries, i.e. nanospheres, nanorods and hollow nanospheres, as well as distinct nanoparticle assemblies. On the one hand these nanostructures are investigated with respect to applications as molecular probes, e.g. in photoacoustic imaging, or as actuators in biomedicine. On the other hand the utilization as fundamental building blocks in nanoelectronic devices is surveyed. Molecules exhibiting distinct functionalities, e.g. anisotropic conductance, or molecules allowing self-organization, e.g. DNA, leading to precisely controllable nanoparticle superstructures are applied. Our characterization involves conventional techniques as IR, NMR, UV-vis, DLS as well as local probe measuring techniques, and investigations on the properties in biological environments.

A further topic deals with the wet chemical synthesis of metal oxide and higher chalcogenide nanostructures, which are applicable as sensor materials, new electrode materials for batteries or as resistive switching elements. In the latter context chemically-based bottom-up approaches for the fabrication of resistively switching nanostructures are explored and aim at the understanding of the switching and its structural consequences of the resistive switching process by using individual nanoparticles as model systems. Furthermore, self-assembly and surface patterning techniques are applied to produce long range order of nanoparticles on solid supports.

Peter Grünberg Institut – Funktionale Nanostrukturen an Oberflächen, Forschungszentrum Jülich

S. Tautz

Our research tackles fundamental issues in the quest towards functional nanostructures at surfaces, with a particular emphasis on nanoelectronics. Since our focus is placed on molecular materials, an important aspect of our work covers the structural investigations and spectroscopy of complex molecular adsorbates on metal, semiconductor and insulator surfaces. Based on these interface studies, the growth of thin films and nanostructures is investigated. Here, our work is directed towards hybrid materials, comprising both organic and inorganic components. Charge transport being the most important function in the context of nanoelectronics, transport experiments on single molecules and nanostructures round off our activities. It is a specific asset of our institute that we combine well-established surface techniques with the development of new experimental methods.

Lehr- und Forschungsgebiet GaN-Bauelementtechnologie, RWTH Aachen

A. Vescan

The research activities of the GaN Device group are focused on the area of group-III nitride device and technology development. The activities include investigation and development of practical technological building blocks for electronic devices, but also address fundamental device issues and limitations. Currently, particular interest is given to high-frequency and high-power device applications, where scaling issues as well as robustness aspects are being investigated. Novel gate dielectric materials are being pursued and their interface properties to GaN are being investigated. Also, alternative heterostructure device concepts are being developed, aimed at enhanced linearity in high-frequency devices as well improved switching behavior in the high-power regime.

Institut für Werkstoffe der Elektrotechnik 2, RWTH Aachen & Peter Grünberg Institut - Elektronische Materialien, Forschungszentrum Jülich

R. Waser

We focus on the physics and chemistry of electronic oxides and organic molecules, which are promising for potential memory, logic, and sensor functions. Our research aims at a fundamental understanding of nanoelectronic functions based on ferroelectricity, piezoelectricity, space charge effects, and electrochemical redox processes and at the elucidation of their potential for future device application. For this purpose, our institute provides a broad spectrum of facilities ranging from dedicated material synthesis, atomically controlled film deposition methods, molecular self-assembly routes, and integration technologies, to the characterization of processes, structures, and electronic properties with atomic resolution.
Integrated Photonics Laboratory, RWTH Aachen

J. Witzens

The realization of photonic components and systems in Silicon allows to realizing complex integrated optical systems at the chip scale. The integrated photonics laboratory is working on the development of Silicon Photonics devices and systems with activities ranging from core device development, system integration, as well as integration with analog circuitry.

I. Physikalisches Institut (IA), RWTH Aachen

M. Wuttig

The institute’s research activities are focused on the development of novel materials for advanced optoelectronic applications. In particular, materials for optical and electronic data storage have been developed in the last few years. For this class of materials, so-called phase change materials, we have established design rules and an atomistic understanding of essential material properties. This work has enabled novel functionalities of phase change materials in applications as non-volatile memories and is part of the SFB 917 (Nanoswitches). Recently, we could demonstrate that some crystalline phase change materials can possess very high levels of disorder, which gives rise to highly unconventional transport properties. Organic materials are a second focus, where we work on routes to tailor material properties for optoelectronic applications ranging from displays, to solar cells and electronic devices.
Selected Research Reports
Electrocoloration of Fe:StoTiO$_3$ for resistive switching made visible by high resolution optical microscopy

V. Havel$^1$, A. Marchewka$^1$, S. Menzel$^2$, S. Hoffmann-Eifert$^2$, G. Roth$^3$, and R. Waser$^{1,2}$

$^1$ Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, Germany
$^2$ Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
$^3$ Institut für Kristallographie, RWTH Aachen University, Germany

SrTiO$_3$ (STO) is regarded as a model material to study the valence change mechanism (VCM) accompanying resistive switching (RS) in the oxide [1]. Prior to RS, typically an initial electroforming step is required. Under high electrical stress, an oxygen-deficient region, referred to as the virtual cathode (VC), is formed. As the electroforming step greatly impacts the device performance and switching variability, its understanding is essential for device optimization. Electroforming is affected by multiple parameters, e.g. voltage, current, temperature, dopant and defect concentrations, ambient gas atmosphere and time. Distinguishing the influence of the particular parameters is a desirable aim and challenging task. Electrocoloration experiments were performed and high resolution transmission light optical microscopy was used to make the redox-processes during electroforming visible. The evolution of the VC is interpreted by drift-diffusion simulation of the time evolution of the oxygen vacancy distribution.

The aim of this study is to obtain in-situ optical images of the transparent Fe:STO single crystals with best possible resolution to get a detailed close-up of the interface of the color regions. In contrast to other optical imaging techniques, our approach uses high resolution transmission light microscopy since this allows for a better insight into the full depth of the sample and delivers information about structural defects in the bulk as well as a good image contrast.

Figure 1 shows designed and constructed custom sample enclosure for the transmission light imaging technique. The enclosure is equipped with high voltage electrical contacts, a sample-embracing heating block, thermocouples for precise temperature control, a gas inlet and bottom top glasses with a heat reflecting coating. Prior to the measurements, the sample is equipped with Pt electrodes on its edges and contacted lengthwise in the enclosure.

During the measurements, a camera on the microscope captures images of the whole sample or close-up images of a sample section with a resolution down to 500 nm, depending on the microscope lens magnification factor.

The sample is connected in series with a high voltage power supply and an ammeter. During the measurement, voltage and current are recorded. With the time photos are captured and subsequently stitched together to sequences and movies, which show the whole electrocoloration process in a time lapse.

Figure 2 depicts a time evolution of the process on a 0.05 wt% Fe:STO single crystal with a size of 5 x 5 x 0.5 mm$^3$, which was biased with 200 V DC voltage and heated up to 300° C. A current compliance of 1 mA was set. The sequence of images demonstrates the time evolution of the observed electrocoloration fronts. The recorded voltage, current and resistance are shown in Figure 3. The process begins with the growth of a dark-brown region at the anode (left in the pictures), whereas at the cathode (right) the color turns from dark to bright-yellow. This evolution of the regions runs smoothly until they reach each other in the middle of the sample. Concurrently, the current through the sample rises and the resistance drops (Fig. 3). The regions are rather homogenous, though their fronts do not propagate evenly through the bulk. This could be assigned to
FIG. 2: Optical images of the Fe:STO 0.05wt% single crystal under DC bias in an ambient temperature 300°C, showing the time evolution of the electrocoloration process.

single-crystal imperfections arisen by the crystal growth (distribution of dopant, defects in the crystal lattice etc.). In this study we focus on the evolution of the envelope of the color front.

The measurement starts in a voltage controlled regime. When the resistance of the sample decrease and the current compliance level is reached, the measurement switches to the current controlled regime (Fig. 2 – approx. 24 hours of runtime). The sample is then supplied by a constant current and the voltage changes proportionally to the sample resistance.

The color changes in Fe:STO are caused by local redox reactions leading to reduced and oxidized forms of the iron dopants [2]. At the anode, Fe turns dominantly into Fe^{4+}, which causes the brownish color [3]. At the cathode, Fe is mainly present in 3+ oxidation state, resulting in a bright yellow color.

To interpret the formation and progression of the color fronts shown in Fig. 2 in terms of oxygen-vacancy movement, one-dimensional simulations of the evolution of the oxygen vacancy distribution were performed using a finite-difference scheme. The oxygen vacancy distribution is calculated by solving the drift-diffusion equation for oxygen vacancies from a set of mass-action law equations and using a Crank-Nicolson time-stepping scheme [4].

Figure 4 shows the calculated time evolution of the oxygen vacancy distribution. Initially, oxygen vacancies of a concentration of $1.4 \times 10^{18} \text{ cm}^{-3}$ are homogeneously distributed within the sample. Upon electrical bias, the oxygen vacancies migrate towards the cathode and accumulate there, forming a highly oxygen-deficient region, i.e. the virtual cathode. The region in front of the anode is depleted of oxygen vacancies. At the oxygen permeable anode, oxygen exchange takes place and additional vacancies are introduced into the crystal. These migrate as well towards the cathode, leading to a growth of the VC towards the anode with time.

FIG. 3: Voltage, current and resistance progression during the measurement. The vertical dotted lines (a)-(i) refer to the times at which the optical images in Figure 2 have been recorded.

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FIG. 4: Simulated time evolution of the oxygen vacancy distribution. The distribution corresponds to the initial progress and matches with the optical images shown in Figure 2. Uniform color turns into three different colored regions, with increasing time the oxygen vacancy gradient in the sample gets steeper and only two differently colored regions are observed in the optical images (Fig. 2c-i).

Electrocoloration of Fe:STO single crystals has been captured using high resolution transmission light microscopy. We have compiled photo sequences of the time evolution of this phenomenon and corresponding voltage, current and resistance values over time. Under moderate excitation conditions and voltages supplied to the sample, the colored regions in the bulk remain smooth without abrupt steps in shape of the regions.

This work was supported in part by the Deutsche Forschungsgemeinschaft under the Collaborative Research Center SFB 917 – Nanoswitches.

Current compliance dependent nonlinearity in TiO$_2$ ReRAMs

V. Rana, F. Lentz, B. Rösgen, and R. Waser

Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany

Nonvolatile redox-based resistive RAM (ReRAM) is considered to be a promising candidate for passive nano-crossbar integration. For this application, a high degree of nonlinearity in I-V characteristics of the ReRAM device is required. In this letter, the nonlinearity parameter as a function of the forming/SET current compliance in a MOSFET integrated TiN/TiO$_2$/Ti/Pt ReRAM device is investigated. The nonlinearity parameter in the ReRAM device improves at the lower SET current compliance. This is due to scaling down the conductive filaments during the forming and the SET process. The nonlinearity is further increased by scaling down the oxide thickness, which is accompanied by a reduction of the switching current.

Switchable metal-insulator-metal (MIM) structures are the key elements for future nonvolatile redox-based resistive RAM (ReRAM) devices [1]. TiO$_2$ based resistive memory elements exhibit excellent properties in terms of data operation and retention [2]. In order to integrate TiO$_2$ ReRAM devices into a passive nano-crossbar architecture, a high degree of nonlinearity in I-V characteristics is required [3], since this property is especially important to prevent a parasitic current flowing through “sneak paths” [4]. The nonlinearity in HfO$_2$ and other metal-oxide ReRAM has been investigated by peer groups and has been controlled by material engineering.

In this paper, we have modulated the nonlinearity in the TiO$_2$ ReRAM devices by using the current compliance during the forming/SET process. The ReRAM devices are highly prone to overshoot phenomena during the electroforming and the SET process, which affect the ReRAM device parameters such as $I_{\text{SET/RESET}}$, $V_{\text{SET/RESET}}$, and nonlinearity, and lead to unstable device operation as reported by Kinoshita et al. [5]. In this study, the parasitic capacitance and the overshoot phenomena are minimized by integrating the ReRAM device with an n-channel MOSFET in a 1T-1R structure. This integrated architecture (1T-1R) has been characterized electrically with quasi-static (QS) voltage sweeps and fast transient pulses. The nonlinearity parameter of the ReRAM device is calculated by dividing $I(V_{\text{RESET}})$ by $I(V_{\text{RESET}}/2)$ at a given pulse width. This definition is deduced from the V/2 addressing scheme for the passive crossbar arrays [4]. The nonlinearity is found to be a function of the SET current ($I_{\text{SET}}$) compliance and increases for lower switching current [5].

A 65 nm CMOS process is used to fabricate n-channel MOSFETs on 300 mm wafers. During the backend processing, a TiN bottom electrode is patterned and planarized on top of W-filled contact vias connecting to the drain junction of the transistor. Afterwards, a 25 nm- or 5 nm-thick TiO$_2$ layer is deposited by reactive sputtering at room temperature. Next, Pt (30 nm)/Ti(5 nm) top electrodes are patterned by e-beam lithography and a lift-off process. These processing steps lead to a layer sequence of TiN/TiO$_2$/Ti/Pt as shown in Fig. 1(a) and (b). The DC and AC characterization was performed under ambient conditions using an Agilent B1500A semiconductor analyzer, an Agilent 81110A pulse-generator and a SRS SR830 lock-in-amplifier.

Generally, a forming process is required to toggle the memory device. In this process, a reduction of the oxide takes place, leading to the formation of an oxygen deficient Magnéli phase filament inside the TiO$_2$. This filamentary conductive path results in the TiN/TiO$_2$/Ti/Pt ReRAM cell in the ON state. Fig. 2(a) shows the electroforming process for the TiN/TiO$_2$(25 nm)/Ti/Pt memory device at different current compliance ($I_{\text{Form}}$).

![FIG. 1: Schematics for (a) DC operation of the TiN/TiO$_2$/Ti/Pt ReRAM device using the MOSFET as current limiter and AC operation is performed by using monitoring contact pad (b) SEM image of the integrated 1T-1R device.](image1)

![FIG. 2: (a) Forming process of 25 nm-thick TiN/TiO$_2$/Ti/Pt ReRAM device. (b) DC I-V characteristics of 25 nm-thick TiN/TiO$_2$/Ti/Pt ReRAM device.](image2)
The forming current was precisely controlled by applying an appropriate $V_{GS}$ to the integrated MOSFET. The corresponding first RESET and the SET process measured by the QS I-V are shown in Fig. 2(b). The maximum $I_{\text{RESET}}$ scales down in proportion to the $I_{\text{SET}}$ and the 25 nm-thick TiO$_2$ ReRAM device can be switched at the lowest $I_{\text{RESET}}$ of 60 µA. The scaling of the $I_{\text{RESET}}$ can be explained by the fact that the MOSFET effectively controls the filament formation inside the ReRAM device and prevents any excessive overshoot current [5]. The $I_{\text{SET}}$ compliance during the switching cycle is directly related to the diameter or numbers of the conductive filaments. As the $I_{\text{SET}}$ compliance decreases, the diameter or number of filaments decreases and leads to the lower $I_{\text{RESET}}$.

For 5 nm-thick TiO$_2$ the switching current is scaled down to 30 µA.

![Image 3](Image 90x522 to 260x599)

**Table 1. Electrical Characteristics of 25 nm TiO$_2$ ReRAM**

<table>
<thead>
<tr>
<th>$V_{GS}$</th>
<th>1.2 V</th>
<th>1.4 V</th>
<th>1.6 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{RESET}}$</td>
<td>60 µA</td>
<td>90 µA</td>
<td>145 µA</td>
</tr>
<tr>
<td>$I_{\text{RESET}}/2$</td>
<td>-63 µA</td>
<td>-100 µA</td>
<td>-131 µA</td>
</tr>
<tr>
<td>$R_{\text{ON}}$</td>
<td>191 kΩ</td>
<td>139 kΩ</td>
<td>63.8 kΩ</td>
</tr>
<tr>
<td>$R_{\text{OFF}}$</td>
<td>5.6 MΩ</td>
<td>1.6 MΩ</td>
<td>1.4 MΩ</td>
</tr>
<tr>
<td>$I_{\text{RESET}}$</td>
<td>-202 µA</td>
<td>-269 µA</td>
<td>-300 µA</td>
</tr>
<tr>
<td>$I_{\text{RESET}}/2$</td>
<td>-27 µA</td>
<td>-40 µA</td>
<td>-125 µA</td>
</tr>
<tr>
<td>Non-linearity</td>
<td>7.4</td>
<td>6.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

A stable quasi-static and pulse SET/RESET switching control in TiO$_2$ ReRAM was demonstrated in the integrated 1T-1R configuration. As the result of the lower parasitic capacitance during electroforming process, stable switching operation at very low reset current of 60 µA for the 25 nm-thick and 30 µA for the 5 nm-thick TiO$_2$ device was achieved. The nonlinearity in the TiO$_2$ ReRAM is modulated as function of the $I_{\text{RESET}}$ and the active device thickness is indispensable to reduce the $I_{\text{RESET}}$ in the ReRAM devices.

In order to mitigate the sneak path current in a passive nano-crossbar array, the higher nonlinearity in the I-V characteristics is desirable. The schematic of the measurement scheme executed to obtain the nonlinearity parameter is shown in Fig. 4. At first, the integrated ReRAM devices were formed and switched to the LRS with the QS sweep and the transistor compliance.

Subsequently, the RESET process is carried out with a voltage pulse of 100 ns width, monitoring the current response of the ReRAM device. For the 25 nm-thick TiO$_2$ device, the DC characteristics and the corresponding AC measurements are shown in Table 1. The highest nonlinearity of $I_{\text{RESET}}/2 = 7.4$ is achieved for the lowest $I_{\text{RESET}}$ (~ 60 µA). These results could be interpreted with the filamentary model [1] in the following way: a higher $I_{\text{RESET}}$ generates a thicker filament in the ReRAM device and leads to enhanced ohmic behavior of the LRS state. To toggle this device back into the HRS or dissolve the filament, the higher current/energy is required.

![Image 4](Image 309x685 to 482x785)

Evidence for multifilamentary valence changes in resistive switching SrTiO$_3$ devices detected by transmission X-ray microscopy

A. Koehl$^1$, H. Wasmund$^1$, A. Herpers$^1$, P. Guttmann$^2$, S. Werner$^2$, K. Henzler$^2$, H. Du$^3$, J. Mayer$^3$, R. Waser$^{1,4}$, and R. Dittmann$^1$

$^1$Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
$^2$Helmholtz-Zentrum für Materialien und Energie GmbH, Berlin, Germany
$^3$Ernst Ruska-Centre (ER-C) for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, Germany
$^4$Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, Germany

Transmission X-ray microscopy is employed to detect nanoscale valence changes in resistive switching SrTiO$_3$ thin film devices. By recording Ti L-edge spectra of samples in different resistive states, we could show that some spots with slightly distorted structure and a small reduction to Ti$^{3+}$ are already present in the virgin films. In the ON-state, these spots are further reduced to Ti$^{3+}$ to different degrees while the remaining film persists in the Ti$^{4+}$ configuration. These observations are consistent with a self-accelerating reduction within pre-reduced extended growth defects.

In recent years resistive switching in transition metal oxides received a lot of research interest due to the proposed application as non-volatile data memory [1]. The resistive switching process is usually attributed to the diffusion of oxygen vacancies driven by the applied voltage and an associated valence change of the transition metal cations. However, explicit detection of valence changes is found rarely in the literature since these changes are expected to take place not within the whole device volume but within small filaments. In order to study the resistive switching process within a complete metal-insulator-metal (MIM) structure by spectroscopic techniques, a significant information depth as well as high lateral resolution is required. Therefore, near edge X-ray absorption fine structure (NEXAFS) - transmission X-ray microscopy (TXM) is a highly suitable tool as it probes the whole film volume with a lateral resolution down to 25nm [2].

In order to enable transmission experiments on our resistive switching SrTiO$_3$ (STO) devices based on an epitaxial thin film, we removed the bulky-STO singly crystal substrates by a specific delamination procedure [3] prior to the measurements. The NEXAFS-TXM study was performed at the U41-XM beamline at BESSY II. Fig. 1a) presents a TXM image at the Ti-resonance with a photon energy of $h\nu=485.0\text{eV}$ of a typical virgin sample. Dark contrast is due to the absorption in the STO thin film. Due to adhesion problems the pads are usually not completely preserved on the support layer, but typically one can find some homogeneous areas of STO as well as several small “spots” of roughly 80-200nm which also show strong Ti contrast. These spots are observed on ON as well as Virgin pads and can be attributed to growth defects induced by the substrate.

FIG. 1: a) TXM-image at $h\nu=485.0\text{eV}$. Dark contrast reveals parts of the SrTiO$_3$ film, which are attached to the support layer. A homogeneous area of the film (marked by right black arrow) as well as a growth defect (marked by left red arrow) is visible. b) Comparison of Ti L-edge spectra of the film and the growth defect reveal a broadening of the $eg$ lines in the defect spectrum [3].
FIG. 2: a) Ti L-edge spectra of several growth defects located within one pad in the ON-state revealing a reduction to Ti$^{3+}$ to different extent. For the top and bottom spectra the $t_2g$-$e_g$ splitting and the corresponding reference material are given. b) Schematic cross-section model for STO films showing growth defects in virgin film and reduction to Ti$^{3+}$ after switching into the ON-state.

The enhanced contrast (darker color in figure 1a)) of the growth defect compared to the film can be explained by an increased sample thickness as additional material is accumulated at the growth defect. The Ti L-edge spectra of the homogeneous film as well as the growth defect reveals the typical absorption characteristic of a STO Ti$^{4+}$ configuration (Fig. 1b) [4]. We furthermore studied pads which have been set into the ON-state. The homogeneous parts of the film have an identical Ti-signature of a pure Ti$^{4+}$ configuration as observed for the virgin area. However, for the spectra of the extended growth defects clear variations occur. In figure 2a) the spectra of several defects within one pad in the ON-state are presented. Significant variations in the spectral shape are apparent, mainly concentrated on the $e_g$ lines. Comparing these spectra to the literature [4], we can assign the variations in spectral shape of the growth defects after switching into the ON-state to a different degree of reduction of Ti$^{4+}$ to Ti$^{3+}$. Based on the spectroscopic results we propose the following model (see figure 2b)): The virgin film consists of a perfect STO thin film containing some extended growth defects. Although the film is slightly disturbed within these growth defects the local structure consists of a perovskite lattice with Ti$^{4+}$ configuration.

Experimentally, on some of these defects a small shift of the $e_g$ peak position is observed. In line with the results observed at the ON-pad, this could be an indication of a small concentration of Ti$^{3+}$ states within the growth defect. Therefore we propose that some of the growth defects are pre-reduced already in the virgin state. In accordance to the current models for VCM type switching we assume, that during forming oxygen is exocorporated from the film. Due to the pre-reduction of the film within the growth defects, which goes along with a higher local n-conductivity, the current density inside the defects is increased relative to the film accelerating the oxygen diffusion by Joule heating. Considering the rather high currents in the mA-regime, significant Joule heating in well conducting paths will lead to self-accelerating of the process and therefore small differences of the starting configuration can lead to large variations in the final composition. This can explain why no reduction is obtained in the homogeneous, defect-free film and that different growth defects will show different degrees of reduction.

In terms of the macroscopic electrical behavior, the different filamentary paths within the growth defects constitute a parallel circuit. While at the beginning several growth defects are reduced, due to the self-accelerating process the current will finally concentrate on one single filament. This filament will carry the main current and dominate the overall pad resistance. Comparison with literature data of the Ti L-edge proves the conservation of the perovskite structure during the reduction without any indications for new phase formations.

Overall we have been able to trace back the resistance change in a resistive switching device to the underlying redox-process and allocate the switching filament to extended growth defects present in the virgin films.

This work was performed within the SFB 917 “Nanoswitches”.

Grazing Incidence Small Angle X-ray Scattering on Resistively Switching SrTiO$_3$

O. Faley$^{1}$, R. Dittmann$^{2}$, R. Waser$^{2,3}$, and U. Klemradt$^{1}$

$^{1}$ II. Physikalisches Inst. B, RWTH Aachen University, Germany
$^{2}$ Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
$^{3}$ Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, Germany

We investigated metal-insulator-metal (MIM) memory cells with Al and Rh top electrodes using grazing incidence small angle X-ray scattering (GISAXS). The roughness of the Al electrodes has been significantly reduced compared to previous work, allowing access to the underlying structures. Measurements on samples with Al electrodes show a signature of structures in the insulating layer similar to previously observed signatures in samples with Ti electrodes.

The development of the next memory generation for information technology is based largely on the understanding of new materials. One promising approach consists of the use of resistively switching oxides, which change their electrical resistance due to the change of valences in the contained cations [1]. This effect can be observed in many transition metal oxides like titanates [2], manganates [3, 4] and zirconates [5]. Since many fundamentals and the exact atomic mechanism of resistive switching are still under debate, structural data are an important contribution to elucidate the physics of resistive switching. In SrTiO$_3$, bipolar resistive switching was first observed more than 10 years ago [2]. Since this material is well understood with respect to its structural and electronic properties, it provides a useful model system to obtain further insight into the physical mechanisms of resistive switching due to valence changes.

We investigated thin oxide films that were lithographically structured into resistively switching memory cells in metal-insulator-metal (MIM) geometry. The memory cells have been laterally patterned into long arrays of electrodes for the optimal coverage by the used grazing angle of 0.6°. The samples were prepared by growing epitaxial Fe-doped SrTiO$_3$ thin films with a Fe concentration of 0.5 at. % on Nb-doped SrTiO$_3$ substrates with a Nb concentration of 0.5 at. %. Pulsed laser deposition was employed to grow epitaxial thin films with a thickness of 20 nm. Ti, Al and Rh were grown as a top layer and structured lithographically into arrays of top electrodes using a positive process. The Ti and Al top layers were sputtered and the Rh layer grown with molecular beam epitaxy with growth parameters optimized for minimum roughness.

The focus of recent work has been on the variation and optimization of the top electrode. The selected material is critical for the electrical characteristics of the memory cells, but also for X-ray experiments. A sketch of conductive filaments formed as a result of voltage-induced changes in the oxygen stoichiometry is shown in Fig. 1. Observed filament diameters vary between 10 nm and several 100 nm, depending on top electrode material [6].

![Fig. 1: Simplified summary of results obtained so far. The detailed geometry of structures observed in samples with Ti and Al electrodes by GISAXS appears to be tapered (see report 2012). The thickness of the active Fe:STO layer is d = 20 nm for all sample (after [6]).](image)

GISAXS measurements were performed at DESY (PETRA III) with a sample-to-detector distance of 4.48 m, a microfocus of 17 μm x 12 μm, a wavelength of 0.95 Å and the detector Pilatus 1M. The MIM-devices were characterized electrically prior to beamtime to ensure that they show the desired electrical behavior. On each sample, arrays of devices were prepared in distinctive electrical states: the high resistive state, the low resistive state and the virgin state (no voltage-induced changes). In samples with Al electrodes, the lower absorption of Al compared to Ti led to a higher intensity of the filamentary signal. In previous measurements the surface roughness of the Al electrodes dominated the GISAXS pattern [6], whereas in recent measurements a lateral structure could be observed, which qualitatively
supports previous results for Ti electrodes [7]. Fig. 2 (a) and (b) show the resulting GISAXS patterns for 10 nm Al/20 nm Fe:STO/Nb:STO samples with different surface roughnesses. Recent measurements on samples with RMS roughnesses below 1 nm [Fig. 2 (b) and Fig. 3] show lateral structures similar to those previously observed in samples with Ti electrodes [6]. This result shows that GISAXS measurements are possible on samples with Al electrodes, providing a second reference system.

![GISAXS patterns](image)

**FIG. 2:** (a) GISAXS-pattern of previous, relatively rough 10 nm Al / 20 nm Fe:STO / Nb:STO devices [6]. (b) Recent measurement on samples with reduced roughness of the Al layer.

In addition, we have used GISAXS to analyze a first sample with Rh top electrodes. The system shows completely unexpected GISAXS patterns with so far the clearest structural correlation with electrical state [Fig. 4]; however, further measurements are required to corroborate an origin from filaments. For a quantitative analysis of the GISAXS patterns, simulations with various software packages [8, 9] and MATLAB are in progress.

![GISAXS patterns](image)

**Fig. 4:** GISAXS on samples with Rh electrodes show distinctive patterns depending on the state of the devices.

The presented research is part of the efforts of the Collaborative Research Group (SFB 917) on the topic of "Resistively Switching Chalcogenides for Future Electronics – Structure, Kinetics and Device Scalability" [10].

Fluorescence lifetime imaging microscopy (FLIM) is introduced as a convenient method for the investigation of the donor distribution in doped oxide materials. Doping in transition metal oxides such as SrTiO$_3$ induces occupied electronic states in the band gap. Since they can be excited to emit fluorescence light, FLIM is particularly suited to map the distribution of these states with a resolution of 1 µm in a fast and efficient way. It is shown that the intensity of the fluorescence signal is directly related to the donor concentration: the intensity increases with the donor content for low concentrations and then decreases at higher concentrations due to the presence of non-radiative recombination centers. By applying FLIM to Nb- and La-doped SrTiO$_3$ Verneuil-grown crystals, distinct inhomogeneities on the micrometer scale were successfully detected demonstrating the potential of this technique to serve as a quality test for oxide crystals and thin films.

Transition metal oxides are promising candidates for future nanoelectronics due to their ability to change their resistance under electric fields rendering the possibility to build memory and logic devices based on this resistive switching effect [1, 2]. In order to produce such devices with a high quality, a control of the growth processes of thin films and single crystals is of enormous importance. The Verneuil process is commonly used to grow oxide single crystals which serve as prototype systems for the investigation of the resistive switching process and furthermore which provide substrates for the deposition of functional thin films. This method is known, in particular, to induce a significant amount of extended defects and inhomogeneities. Hence, characterisation techniques are called for which are capable of mapping the inhomogeneous distribution of dopants and the related effects on the local electronic structure. Even though FLIM is a well-established technique in life science, we will present its potential to fulfil the task at hand by exemplarily mapping the inhomogeneous distribution of the electronic structure in Nb- and La-doped crystals [3].

At first global fluorescence spectra were recorded on SrTiO$_3$ single crystals with different Nb concentrations, in order to correlate the measured fluorescence signal qualitatively with the local donor concentration. The spectra are presented in Fig. 1. It can be seen that undoped SrTiO$_3$ did not emit any fluorescence while the crystal doped with 0.1 wt% showed a significant fluorescence signal with high intensity. At higher doping concentration, a decrease of the intensity of the fluorescence signal with the doping concentration can be observed.

FIG. 1: Fluorescence spectra measured on Nb-doped SrTiO$_3$ single crystals with different Nb-content after excitation with a 325 nm HeCd laser with a power density of 0.1W/cm$^2$.

This behavior can be understood regarding the electronic structure of SrTiO$_3$. While Ti is in the oxidation state +4 in undoped SrTiO$_3$, donor doping leads to an oxidation state change to +3 and a fluorescence involving the corresponding energy level in the band gap close to the conduction band can be excited. At higher donor concentrations, the electron density in the conduction band increases leading to a suppression of the fluorescence signal since non-radiative Auger processes become more relevant.
Since there is a direct correlation between the fluorescence signal and the electronic structure with respect to the Ti valence +3, the local distribution of the electronic structure was measured on doped single crystals as shown exemplarily for two Nb-doped crystals in Fig. 2. In order to bridge the band-gap of SrTiO$_3$ with infrared light, two-photon excitation was used. While scanning the crystal with an infrared laser beam generated by a Ti:Sa-laser (100 fs, 80 MHz), the fluorescence signal was recorded by a photomultiplier in non-descanned configuration. Using a fitting procedure, maps of the intensity and the lifetime of the fluorescence were calculated. In both maps, the crystal doped with 0.7 % Nb showed a characteristic inhomogeneous cluster-like structure on the micrometer scale interspersed with long-range lines. As can be seen in the inset of Fig. 2A, the lifetime within these lines was reduced by more than 40%. Two regions were revealed with significant differences in the electronic structure.

The crystal doped with 5 % Nb, which had a lower quality with respect to inhomogeneities exhibited striped structures with a total thickness of 50-100 µm in the maps of the fluorescence (Fig. 2B). These structures show an additional sub-structure with smaller stripes with a thickness of 3-10 µm. The fluorescence maps were compared with maps of the Nb distribution measured directly by means of secondary ion mass spectrometry (SIMS). A direct correspondence between the two methods can be recognized. This illustrates that the inhomogeneities in the electronic structure that were detected by FLIM were caused by an inhomogeneous donor distribution in the single crystals, which is furthermore supported by the fact that similar inhomogeneities were also detected in La-doped SrTiO$_3$.

The proof of the existence of inhomogeneities on the micrometer scale is particularly relevant for the use of donor-doped single crystals as metallic substrates for the growth of oxide thin films. If devices were prepared using the crystals investigated, the properties of the devices would depend on their position on the substrate. This emphasizes the need for the investigation of alternative materials and methods for high-quality substrates. In order to determine the donor distribution in oxide materials, we therefore propose the establishment of a characterization technique employing FLIM, which has the potential to fulfill these requirements in a fast and efficient way.

This work was supported in part by the Deutsche Forschungsgemeinschaft under the Collaborative Research Center SFB 917 – Nanoswitches.


Generic relevance of counter charges for cation-based nanoscale resistive switching memories

S. Tappertzhofen¹, R. Waser¹,², T. Tsuruoka³, T. Hasegawa³, M. Aono³, and I. Valov²

¹ Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, Germany
² Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
³ WPI-MANA, National Institute of Materials Science, Tsukuba, Japan

Resistive switching memories (ReRAMs) are the major candidates for replacing the state-of-the-art memory technology in the future nanoelectronics. We show that in the context of many cation based ReRAMs, the formation of mobile ions proceeds in parallel to reduction of moisture, supplied by the ambient. The outcome of this study highlights the hitherto overlooked necessity of a counter charge/reaction to keep the charge electro-neutrality in the cation transporting resistive switching thin films.

To study in detail the impact of moisture on Cu redox processes, we performed CV measurements at different water partial pressures pH₂O (Fig. 1). Particularly, we analyzed the impact of pH₂O on the concentration of ions c_con generated during the sweeping. It must be emphasized that both the concentration of Cu ions c_Cu⁺, as well as hydroxide ions OH⁻ c_OH⁻ are contributing equally to c_con. Details on the shape of the CV curves can be found in [3].

FIG. 1: Impact of moisture on Cu z+/Cu redox processes. CV curves in hydrated nitrogen atmosphere (pH₂O = 1 hPa to 23 hPa). (Redrawn from [2])

The concentration c_con can be estimated by integration of the current during the sweep and the cell geometry. The diffusion coefficient D is derived using the Randles-Sevcik equation [3]. Increasing of pH₂O during anodic oxidation results in an increase of c_con (Fig. 2a), because the introduction of the counter charge at the Pt/SiO₂ interface seems to be the limiting process for anodic oxidation. This relation unequivocally reveals that hydroxide ions are acting as counter charge rather than electrons. At higher water partial pressures more OH⁻ can be reduced at the Pt/SiO₂ interface and respectively, a higher amount of Cu⁺ can be dissolved. The high local concentration of Cu²⁺ ions leads to ion-ion interactions and increasing the partial pressure of water results in a decrease of the diffusion coefficient D (Fig. 2b) as in the case typical for concentrated solution conditions [3]. However, the estimated diffusion coefficient for Cu ions is magnitudes of orders higher compared to the extrapolated values of bulk SiO₂ at room
temperature. We contribute the higher diffusion coefficient mainly to the nano-porous structure of the deposited SiO$_2$ layer. The diffusion may be additionally increased due to an impact of moisture within the SiO$_2$ and an electric field enhancement.

![FIG. 2: (a) Ion concentration $c_{\text{ion}}$ dependence on $p\text{H}_2\text{O}$ at constant sweep rates, respectively. The ion concentration depends on the water partial pressure during the anodic oxidation sweep. (b) Diffusion coefficient $D$ calculated by the Randles-Sevcik equation and depending on the water partial pressure. (Redrawn from [2])](image1)

The incorporation of charges separated at the both interfaces i.e., Cu$^{2+}$ at the Cu/SiO$_2$ interface (I) and OH$^-$ at the SiO$_2$/Pt interface (II) leads to a formation of an emf (electromotive force) within the ECM cell. The emf $V_{\text{emf}}$ voltage is given by Nernst potentials $V_{\text{N}}$ contribution and a diffusion potential $V_{\text{d}}$ [2]. This emf voltage results further in a measurable cell voltage $V_{\text{Cell}}$ depending on the ionic transference number of SiO$_2$. The cell voltage has been measured at different water partial pressures $p\text{H}_2\text{O}$ in nitrogen atmosphere as depicted in Fig. 3.

![FIG. 3: $V_{\text{Cell}}$ dependence on the water partial pressure in nitrogen atmosphere. Each point corresponds to a different $p\text{H}_2\text{O}$ value. (Redrawn from [2])](image2)

$V_{\text{Cell}}$ was adjusted prior to the experiment by a single linear anodic oxidation sweep. The ion concentration of both cations and OH$^-$ is believed to be constant during the experiment. The highest value for $V_{\text{Cell}}$ is measured in anhydrous nitrogen atmosphere. When $p\text{H}_2\text{O}$ is increased a decrease of $V_{\text{Cell}}$ is observed as theoretically expected from the influence of $p\text{H}_2\text{O}$ on the Nernst and diffusion potentials [2]. Moreover, $V_{\text{Cell}}$ can be reversibly tuned (increased or decreased) depending on the particular water partial pressure. Hence, $p\text{H}_2\text{O}$ and therefore, the water molecules incorporated into SiO$_2$ do not significantly increase the ion mobility (due to solvent effects) and the Cu$^{2+}$ and OH$^-$ ion concentration gradients and respectively, the driving force for $V_{\text{Cell}}$ are not changed.

![FIG. 4: Schematic cross section of Cu/SiO$_2$/Pt cell showing the penetration of moisture into the SiO$_2$ thin film. By change of the water partial pressure $p\text{H}_2\text{O}$ moisture is likely penetrating into SiO$_2$ from the lateral sides. (Redrawn from [2])](image3)

These results underline the importance of a counter charge/reaction. Without a counter charge/reaction no anodic oxidation can take place and thus, the resistive switching effect is not observed. We have verified that water is mainly supplying the required counter charge(s) for anodic oxidation and hence, resistive switching rather than enhancing the Cu$^{2+}$ ion mobility in SiO$_2$ thin films, which would result in an irreversible decrease of $V_{\text{Cell}}$ by increase of $p\text{H}_2\text{O}$. Electrons alone seem to play an inferior role as counter charges required for keeping the electro-neutrality, because anodic oxidation is not observed in anhydrous atmosphere. We assume moisture is likely penetrating from lateral sides as depicted in Fig. 4. However, resistive switching experiments [4] indicate a $p\text{H}_2\text{O}$ equilibration in the complete SiO$_2$ thin film thus, even underneath the top electrodes. This complies with our observation that the $V_{\text{Cell}}$ equilibration can take up to several hour depending on the change of ambient water partial pressure.

In this study, we have clearly demonstrated that a counter charge/reaction is inevitably required to enable anodic oxidation. Moisture supplying this counter charge/reaction is playing an important role during the electrochemical oxidation of Cu ions being responsible for the filament formation and therefore, for resistance transition in SiO$_2$ based ReRAM cells.

Switching kinetics of electrochemical metallization memory cells

S. Menzel\textsuperscript{1}, S. Tappertzhofen\textsuperscript{2}, R. Waser\textsuperscript{1,2}, and I. Valov\textsuperscript{1}

\textsuperscript{1}Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
\textsuperscript{2}Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, Germany

The strongly nonlinear switching kinetics of electrochemical metallization memory (ECM) cells are investigated using an advanced 1D simulation model. It is based on the electrochemical growth and dissolution of a Ag or Cu filament within a solid thin film and accounts for nucleation effects, charge transfer, and cation drift. The model predictions are consistent with experimental switching results of a time range of 12 orders of magnitude obtained from silver iodide (AgI) based ECM cells. By analyzing the simulation results the electrochemical processes limiting the switching kinetics are revealed.

Electrochemical metallization memory (ECM) cells are a promising candidate for next generation non-volatile, high speed and highly scalable memory cells \cite{1,2}. The switching is attributed to the electrochemical growth and dissolution of a Cu or Ag nano-sized filament. Typically, ECM cells consist of a Cu or Ag active electrode, an ion conducting switching layer (SL) and an inert electrode. During the SET process a positive potential is applied to the active electrode which is oxidized. Ag or Cu cations are driven out of the active electrode and migrate through the switching layer. At the inert cathode the cations are reduced and a metallic filament grows towards the anode resulting in a low resistive state (LRS). To RESET the device to a high resistive state (HRS), the voltage polarity is reversed and the filament dissolves. Here we report on an advanced simulation model for the switching kinetics in ECM cells \cite{3} accounting for all factors influencing the switching kinetic: i) the nucleation process prior to filamentary growth, ii) the electron transfer reaction occurring at the metal/SL interfaces, and iii) the ionic transport within the SL.

Fig. 1 illustrates all relevant electrochemical processes involved in resistive switching. The formation of the metallic filament on foreign substrate necessarily starts with a nucleation. The formed nucleus, which consists of an integer number of metal atoms, has to achieve a critical cluster size \( N_C \). The nucleation time under constant applied voltage (nucleation overpotential \( \eta_{\text{nuc}} \)) is given by

\[
t_{\text{nuc}} = t_{0,\text{nuc}} \exp \left( \frac{\Delta G_{\text{nuc}}}{k_B T} \right) \exp \left( - \frac{(N_C + \alpha) e}{k_B T} \eta_{\text{nuc}} \right).
\]

Here, \( t_{0,\text{nuc}} \), the Boltzmann constant \( k_B \), the temperature \( T \), the elementary charge \( e \), the charge number \( z \) involved in the cation reduction,

\[
\eta_{\text{nuc}} = \frac{\Delta G_{\text{nuc}}}{k_B T} + \eta_{\text{tr}} + \Delta G_{\text{ele}} - \eta_{\text{ele}}.
\]

and depends on the electron transfer overpotential \( \eta_{\text{et}} \). The activation barrier \( \Delta G_{\text{et}} \) is included in the exchange current density \( j_{0,\text{et}} \) given by

\[
j_{0,\text{et}} = z e c k_0 \exp \left( - \frac{\Delta G_{\text{et}}}{k_B T} \right).
\]

The exchange current density \( j_{0,\text{et}} \) depends also on the concentration \( c \) of ions at the interface and a rate constant \( k_0 \). The ion transport (B) within the insulating layer and the corresponding current density can be calculated by the Mott-Gurney Law:

\[
j_{\text{ion}} = \frac{z e c k_0}{k_B T} \exp \left( - \frac{\Delta G_{\text{ion}}}{k_B T} \right) \exp \left( - \frac{z e}{k_B T} \eta_{\text{ion}} \right).
\]
Here $a$ is the mean ion hopping distance, $f$ the attempt frequency, $\Delta G_{\text{hop}}$ the migration barrier height, $c$ the ion concentration, and $E$ the applied electric field. The filament growth/dissolution (E) and thus the change of $x$ can be described using Faraday's law:

$$\frac{\partial x}{\partial t} = -\frac{M_{\text{Me}}}{ze\rho_{\text{Me}}} J_{\text{Me}e}.$$ 

Here, $J_{\text{Me}e}$ is the ionic current, $z$ the charge transfer number, $M_{\text{Me}}$ the atomic mass and $\rho_{\text{Me}}$ the mass density of deposited metal. The tunneling current $I_{\text{Tu}}$ can be calculated according to Simmons as

$$I_{\text{Tu}} = \frac{3CK e^2}{2\hbar} \exp\left(-\frac{4\pi x}{\hbar} K\right) A_{\text{fil}} V_{\text{Tu}},$$

where $K = \sqrt{2m_{\text{eff}} \Delta W_0}$ and $m_{\text{eff}}$ and $\Delta W_0 = 3.6$ eV are the electron effective mass and the tunneling barrier, respectively.

Figure 2 depicts the equivalent circuit diagram of the simulation model. The simulation of the switching kinetics is divided into two steps: nucleation and filamentary growth. First the nucleation is calculated and then the differential equation is solved using the simulation model. The used simulation parameters are given in Table 1.

![Schematic of the switching model with equivalent circuit diagram.](image)

**FIG. 2:** Schematic of the switching model with equivalent circuit diagram. A switching layer of thickness $L$ is sandwiched between the active top electrode and the inert bottom electrode. A cylindrical filament (the form is arbitrary chosen for simplicity) grows within the electrolyte film and modulates the tunneling gap $x$ between the filament and the active electrode. In the switching layer both ionic and electronic current paths are present, respectively. (Redrawn from [3]).

To study the switching kinetics simulations were conducted using the presented ECM model. As excitation voltage pulses with varying amplitude $V_{\text{app}}$ and a rise time of $t_{\text{rise}} = 5$ ns are used. The switching time $t_{\text{sw}}$ is defined as the point in time, where a current compliance $I_{\text{cc}} = 100$ nA is reached. Figure 3 shows the simulated switching kinetics as a function of the applied voltage for different temperatures compared to experimental data obtained from 20 nm thick AgI based ECM cells [3]. The simulated data is displayed using solid lines and the experimental data using squares. Using the simulation model the processes limiting the switching kinetics can be identified. It can be distinguished between three different regimes: for low voltages the nucleation processes limits the switching speed (I), for intermediate voltages the electron-transfer reaction (II) and at high voltages a combination of electron-transfer reaction and ion hopping.

![Pulsed SET switching kinetics of the AgI-based ECM cell for different ambient temperatures $T = 298$ K (blue), $323$ K (red), $348$ K (black) and $373$ K (light green). The simulated data is displayed using solid lines and the experimental data using squares. I, II, III mark the nucleation limited, the electron transfer limited and the mixed control regime, respectively. Details on statistical variation can be found in 29. (Redrawn from [3]).](image)

**FIG. 3** Pulsed SET switching kinetics of the AgI-based ECM cell for different ambient temperatures $T = 298$ K (blue), 323 K (red), 348 K (black) and 373 K (light green). The simulated data is displayed using solid lines and the experimental data using squares. I, II, III mark the nucleation limited, the electron transfer limited and the mixed control regime, respectively. Details on statistical variation can be found in 29. (Redrawn from [3]).

In conclusion, we presented a physical simulation model for the switching kinetics in ECM cells accounting for all relevant rate limiting processes and variable experimental conditions.

A Static CMOS-Amplifier Calibration Scheme based on Nanoelectronic Resistive Switches

A. Heittmann and T.G. Noll
Electrical Engineering and Computer Systems, RWTH Aachen University, Germany

A static sense amplifier calibration scheme is proposed which significantly mitigates the impact of CMOS process variability on the trigger voltage variation. The area-efficient calibration circuit incorporates resistive switches (RS) as non-volatile and multilevel processing elements. To evaluate the circuit performance extensive Monte-Carlo simulations were executed considering CMOS device variability, noise, and variability of RS’s switching kinetics.

Over the past years research in the area of resistive switches (RS) has turned out several favorable properties of RS which marks them as promising candidates for use as memory elements in future non-volatile memories, programmable logic and specialized applications, for example, artificial neural networks. On one hand, their comparatively simple technological setup may help to master the technological challenge for scaling nanoelectronic systems beyond the 10nm node since many RS devices can be implemented with a minimum area occupation of 4F² per device (F: lithographic resolution). On the other hand, many RS devices provide multi-level capabilities [1,2] allowing for the non-volatile storage of several bits in a single cell and can be programmed as well as re-programmed by specific electrical stimuli.

Due to the passiveness of RS the application of RS in nanoelectronic circuits requires active circuit components such as amplifiers and drivers. From the point of view of circuit reliability as well as circuit robustness variability effects in scaled circuits are seen as a limiting factor for the performance of nano-scaled circuits. In bulk MOS devices effects of random discrete dopants (RDD) [3], work function variation (WFV), line edge roughness (LER) and random telegraph noise (RTN) induced by trapped charges account for a random shift in the threshold voltages as well as current factors of individual transistors.

One essential component of an RS-based memory array is the sense amplifier which converts and amplifies small cell signals obtained from the cell array into signals comprising full swing for further processing. A typical strategy to lower power consumption in the cell array is to decrease the signal swing of the cell signal to the lowest possible level. Then, however, the detection of the cell’s state becomes more and more difficult in the presence of device variability and noise.

Particularly, in conventional amplifier designs the ability to reliably discriminate states depends significantly on the matching of individual transistor pairs, i.e. the electrical properties of particular transistor pairs should be similar as much as possible. For future CMOS devices in the nanometer regime this particular attribute can no longer be presumed in the presence of variability.

For nanoscale circuits we propose a new circuit technique which is able to cope with the impact of device variability. Instead of optimizing the matching properties of particular transistor pairs by design (i.e. by means of layout and area optimization) mismatch is tolerated. The resulting biased operation points are individually as well as adaptively shifted. The here involved auxiliary circuits need to be as small as possible. While for classical CMOS circuits such a technique can only be realized by leaky storage elements (i.e. capacitors which need to be refreshed at the beginning of each operational cycle) a static calibration scheme is proposed here which is based on nanoelectronic resistive switches. In particular, the proposed scheme exploits the multilevel capabilities as well as the non-volatility of RSs.

FIG. 1: Calibration circuit (a), calibration loop (b) and operation with calibrated trigger voltage (c).
The two operational modes of the calibration circuit are shown in Fig. 1. A voltage divider formed by two RSs (Fig. 1a) delivers a local reference voltage to a differential amplifier A. For an uncalibrated amplifier the trigger voltage appears to be variable, cf. Fig. 2, due to local variations (the gray curves in Fig. 2) which results in a reduced signal margin and potentially causes state detection errors in the presence of additional noise.

![FIG. 2: Reduced signal margin resulting from offset and noise.](image)

By increasing or decreasing the conductances GL and/or GU using electrical stimuli (supplied either by a current mirror or a switched voltage source) the reference voltages - and hence the trigger voltage - is shifted by discrete increments. By embedding the calibration circuit in a control loop (cf. Fig. 1b) the trigger voltage can be set with a precision up to a limit which is given by the present noise and the variability of the switching kinetics of the RS devices. After calibration the control loop is disconnected and the circuit operates with the desired performance. Recalibration is only necessary if the reference voltage changes due to incidental events (which expected rate needs to be assessed in a device-dependent way) or aging.

In the proposed circuit RS devices were used which are based on the electrochemical metallization effect (ECM) [2]. While the ECM switching kinetics is determined by a process of forming a nanoscale filament variability of the filament growth affects the residual variation of the reference voltage.

![FIG. 4: a. Empirical histogram of reference voltage overshoot based on Monte-Carlo simulation. b. Amplifier gate area vs. achievable variation of the trigger voltage, limited either by static variability, RTN (for the fully calibrated amplifier), and thermal noise.](image)

The statistical properties of the circuit's transfer characteristics are shown in Fig. 3 for various operational parameterizations (i.e. programming voltage, pulse width), and were obtained by extensive Monte-Carlo simulations using both a statistical model for the ECM switching kinetics [4] as well as a statistical model for the transistor variability. While the precision of the reference voltage is inversely related to the pulse width, resolution of the adaptation process depends on the trigger voltage (VPF, cf. Fig. 3b) the inherent resolution of the reference voltage is given by the discrete deposition of single atoms on the device filament, cf. Fig 4a. Finally, in the case of reaching minimal voltage steps, noise limits the effective resolution. In the case of random telegraph noise (RTN), which is assumed to be the dominant factor for the amplifier performance, an active gate area reduction by one order of magnitude (factor of 10) is possible for a specified allowed variation of the trigger voltage, cf. Fig. 4b.

Ferroelectric translational antiphase boundaries in nonpolar materials

X.-K. Wei\(^1,2\), A.K. Tagantsev\(^1\), A. Kvasov\(^1\), K. Roleder\(^3\), C.-L. Jia\(^2\), and N. Setter\(^1\)

\(^1\)Ceramics Laboratory, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland
\(^2\)Peter Grünberg Institut-5, Forschungszentrum Jülich, Germany
\(^3\)Institute of Physics, University of Silesia, Katowice, Poland.

Ferroelectric materials are heavily used in electro-mechanics and electronics. Inside the ferroelectric, domain walls separate regions in which the spontaneous polarization is differentially oriented. Properties of ferroelectric domain walls can differ from those of the domains themselves, leading to new exploitable phenomena. Even more exciting is that a non-ferroelectric material may have domain boundaries that are ferroelectric. Many materials possess translational antiphase boundaries, which could be interesting entities to carry information if they were ferroelectric. Here we show first that antiphase boundaries in antiferroelectrics may possess ferroelectricity. We then identify these boundaries in the classical antiferroelectric lead zirconate and evidence their polarity by electron microscopy using negative spherical-aberration imaging (NCSI) technique. Ab initio modelling confirms the polar bi-stable nature of the walls. Ferroelectric antiphase boundaries could make high-density non-volatile memory; in comparison with the magnetic domain wall memory, they do not require current for operation and are an order of magnitude thinner.

Domain boundaries make an intriguing and challenging research subject because of their peculiar properties and promising perspective in designing nanoelectronic devices. One typical paradigm is the discovery of electronic conductivity at ferroelectric domain walls in multiferroic oxides such as BiFeO\(_3\) \(^1\). Charged domain walls in the ubiquitous ferroelectric BaTiO\(_3\) showed electronic-gas-like conductivity while the individual domains remained excellent insulators \(^2\). Large photovoltages can be generated by domain walls, which become attractive for photovoltaic devices \(^3\). These properties are particularly attractive because domain walls can be created, annihilated, rewritten, and displaced electrically inside the material, potentially leading to agile nanoelectronics.

Antiferroelectric behavior of a crystal can be rationalized in terms of a simple two-instability Landau-type theory. The dielectric anomaly is attributed to the softening of a transverse optic polar mode at the \(\Gamma\)-point of Brillouin zone. The Curie temperature \(T_c\) for this softening is close to but lower than the transition temperature \(T_s\). Such mode softening is identical to that in ferroelectrics. However in contrast to ferroelectrics, in antiferroelectrics, this mode softening is interrupted at \(T = T_s\) by a repulsive interaction between the polarization and the structural order parameter appearing at the transition. If this coupling is strong enough, the frequency of the antiferroelectric soft mode increases on cooling below \(T_s\). This entails a decrease of the dielectric constant with lowering temperature below the transition. Such evolution of the dielectric constant with temperature is typical for antiferroelectrics.

The following free energy expansion in terms of the polarization, \(p\), and the structural order parameter, \(\xi\),

\[
F(p, \xi) = \frac{A}{2} (T-T_s) p^2 + \frac{\eta}{2} p^2 \xi^2 + F_A(\xi)
\]  

readily reproduces the above scenario for antiferroelectricity. Here the coefficient \(\eta > 0\) controls the repulsive biquadratic coupling between the polarization and the structural order parameter. The transition at \(T = T_s\) is described by the contribution to the free energy \(F_A(\xi)\), implying softening of a lattice mode associated with the order parameter \(\xi\). The corresponding critical temperature, \(T_c\), should be equal to \(T_s\) or slightly lower than \(T_s\). Using the equation of state for polarization \(\partial F / \partial P = E\) (\(E\) is the electric field), for the high-temperature phase (with \(\xi = 0\)), Equation (1) yields the Curie Weiss law \(\chi = 1/(T-T_s)\) for the dielectric susceptibility defined as \(\chi = dP/dE\).

Similarly, for the low-temperature phase where the order parameter of the transition, \(\xi\), acquires a spontaneous value of \(\xi_s\), the susceptibility can be found in the form

\[
\chi = \frac{1}{A(T-T_s) + \eta \xi^2_s}
\]

Equation (2) corresponds to the antiferroelectric-type anomaly if \(A(T-T_s) + \eta \xi^2_s\) increases on cooling. This is possible if the increase of \(\xi_s\) with lowering temperature dominates the behavior of this term. Such a condition can be assured by a large enough coupling constant \(\eta\).

At high temperatures, PZ has the ideal cubic perovskite structure shown in Figure 1A. After cooling through a first order phase transition at \(T_c\ \sim\ 500\) K, the structure changes from cubic \(\bar{m}3\bar{m}\) to orthorhombic \(mmm\). The structural changes at the transition can be presented as a combination of
displacements in two lattice-modes [4], one corresponding to the Σ point (the wave vector \( k_\Sigma = 2\pi/a_c (1/4,1/4,0) \); \( a_c \) is the cubic lattice constant) in the Brillouin zone and the other corresponding to the R point (\( k_R = 2\pi/a_c (1/2,1/2,1/2) \)). The distortions associated with the Σ point are mainly related to displacements of lead ions (Figure 1B) while those associated with the R point derive from antiphase rotations of the oxygen octahedra (Figure 1C) about the crystallographic axes of the cubic phase. Thus, the transition is governed by a mixed order parameter, containing Σ-point and R-point-related components.

Figure 1: Structure of lead zirconate. A. The cubic unit cell. Lattice modes relevant to the phase transition into the orthorhombic phase: B. Lead displacements in the Σ-mode. C. Oxygen-octahedron rotations in the R-mode. In B and C, the projections of the orthorhombic unit cells onto the ab plane (rectangles) are shown.

Figure 2A is a dark-field image of a PZ crystal, showing translational domains separated by domain walls. These translational domains correspond to a single orientational domain. The topological nature of the domain walls, allows reactions between them, Figure 2B shows a high-resolution TEM image of an APB. A \( \pi \) phase shift of the order parameter occurs between the two highlighted unit cells. The identity of these two unit cells can be checked with lead displacements. Passing a pair of rows in the [010] direction, the sign of lead displacements alternates as shown with the blue/pink arrows in Figure 2B. The number of lead containing rows between the two highlighted unit cells is 10 (and not a multiply of 4), evidencing the \( \pi \) phase shift and the existence of the APB region. Based on image simulation, the atomic positions corresponding to the experimental image are obtained from the model.

Figure 3C shows a violation of the correlation in the antipolar in-plane Pb displacements in the APB area. Due to the depolarizing effect, polarity is expected only in the boundary plane, i.e along the [100] orthorhombic axis. Scrutinizing the x-atomic displacements shown in Figure 3D, we find a systematic unipolar displacements of Zr in 7 elementary cubes (pseudo-cubic unit cells) with an average value of about 8 pm. As Figure 2E shows, calculation reveals that the spontaneous polarization inside the APB is up to 14 uC/cm². Re-arrangement of the oxygen atomic positions at the APB area, revealing breaking of the antiphase correlated rotation of the octahedra, is also observed. Within the accuracy of the experiments, width of the APB can be evaluated as one to two orthorhombic unit cells along [010] direction. The experimental results are confirmed by first-principles calculations [5].

Figure 2: Morphology and atomic details of translational boundaries in antiferroelectric PZ. A. Dark-field image shows morphology of the translational. Topological features of these boundaries are marked by red circles. B. Atomic-resolution image of an APB between two translational domains recorded under NCSI conditions along [001] direction. The APB is evidenced by the conflict of half a unit cell in between these two domains. C-D. Averaged displacements of Pb and Zr atoms with respect to the cubic atomic positions along x direction as function of the plane positions along y direction. E. Dipole moment density obtained by averaging the dipole moments in a “sliding” orthorhombic unit cell and plotted as a function of the centers of the sliding cells. Squares: in-plane (x) components parallel to the wall; circles: out-of-plane (y) components normal to the wall.

Ferroelectric antiphase domain boundaries in antiferroelectrics can be viewed as functional elements, 1-10 nm wide, which carry information. Unlike twin domain walls, the polar translational walls are non-ferroelastic, which makes them strain-free, thus even more appealing for potential ultra-high density mobile information-carrying elements.

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Stability of spin-driven ferroelectricity in the thin-film limit

A. Glavic1, J. Voigt1, E. Schierle2, E. Weschke2, C. Becher3, M. Fiebig3, and T. Brückel1

1 Jülich Center for Neutron Science-2/Peter Grünberg Institut-4, Forschungszentrum Jülich, Germany
2 BESSY II, Helmholtz-Zentrum Berlin, Germany
3 Department of Materials, ETH Zürich, Switzerland

We demonstrate spin-spiral-induced ferroelectricity in epitaxial TbMnO3 films grown on YAlO3 substrates down to a film thickness of 6 nm. The ferroelectric polarization is identified by optical second harmonic generation (SHG). Using X-ray resonant magnetic scattering (XRMS) we directly prove the existence of a non-collinear magnetic structure in the ferroelectric phase and thus bulk-like multiferroicity. The electric-field-induced reversal of the magnetic domains along with the reversal of the ferroelectric polarization evidences the rigid coupling of magnetic and ferroelectric order and hence, a "giant" magnetoelectric effect in the films.

Competing magnetic interactions in crystals can lead to sinusoidal, helical, or cycloidal spin structures whose periodicity does not follow the periodicity of the lattice. The inherent competition and the low symmetry of such spiral-type structures is a rich source of exotic physical phenomena such as magnetically induced ferroelectricity, complex magnetic excitations like electromagnons and helimagnons or pronounced spin-torque effects. The strong coupling between the magnetic and electric order parameters holds also the potential of technical applications, e.g. four state memories or storage devices with magnetic readout and electrical writing exhibiting better energy efficiency.

The prototypical bulk multiferroic TbMnO3 develops a ferroelectric polarization, when the magnetic structure changes from a longitudinally modulated structure into a chiral structure [2]. The loss of inversion symmetry associated with this transition provides the necessary condition for ferroelectric order [3]. First attempts to realize thin films of TbMnO3 did not exhibit a ferroelectric polarization, but instead showed a strain-induced formation of a macroscopic magnetization exemplifying the subtle balance between the different interactions [4].

We have grown our samples on YAlO3 (100) oriented substrates, which match the a and b lattice constants of bulk TbMnO3 nearly perfectly, resulting in a very low strain present in the film. Using the pool of in-house characterization methods we combined the information from x-ray reflectivity, Rutherford backscattering spectroscopy, atomic force microscopy and SQUID magnetometry to optimize the growth conditions for TbMnO3 thin films.

To establish the magnetic structure for a series of thin films with varying film thickness, we employed X-ray Resonant Magnetic Scattering (XRMS). Here we use two unique features of the resonant magnetic scattering cross section: (i) it is element sensitive and hence we can probe the magnetic order of the Mn ions and the Tb ions independently, (ii) using polarized x-ray photons the scattering depends on the relative orientation of the magnetic moments in the sample with respect to the x-ray polarization and the direction of the scattered x-ray beam.
Fig 1a) shows the temperature evolution of the different components of the magnetic moment of the Mn ions and the Tb ions. Clearly the $b$-component of the Mn magnetic moment orders at $T_N = 43$ K, similar to the bulk behavior. The ordering of the $c$-component sets in at $T_{c} = 26$ K again very similar to bulk behavior. And finally we could observe the Tb order with a different propagation vector $(0\ T_0\ 0)$ below $T_{N\text{B}}=\text{11}\ \text{K}$. We find the same behavior for all investigated film thicknesses ranging from 6 nm to 100 nm. Thickness dependent differences are the correlation lengths of the magnetic order, which are in all cases given by the film thickness and the way the periodicity of the sinusoidal or cycloidal structure evolves with temperature. Thinner films tend to have significantly larger changes compared to thicker films or bulk indicative of the strong sensitivity to even small epitaxial strain.

The independent proof of ferroelectric order was established by Second Harmonic Generation (SHG): If the sample is illuminated with intense laser light, non-linear optical effects lead to the emission of light having twice the frequency or half the wavelength of the original light. Again the polarization of the initial and final light beam gives the hint to the physical origin of the generated light. Fig. 1b) shows the SHG intensity originating from an electric polarization present in the sample. It appears exactly at the same temperature, when the second component of the magnetic moments order and diminishes as the order of the Tb moments increases. The symmetry of the non-linear susceptibility measured by rotating the incident and outgoing polarization fits very well the expected direction of the ferroelectric polarization.

From these independent measurements we can conclude that the reduction of epitaxial strain allows the formation of multiferroicity in thin TbMnO$_3$ films. To manipulate the cycloidal order with an electric field manifesting the strong magneto-electric coupling we applied a new method developed from the colleagues at BESSY II [5]. A strong electric field in the plane of the films is created by the point charges at the position where the very intense photon beam from the synchrotron hits the sample due to the photoelectric effect. This field aligns the polarization on one side of the burn point in one direction and on the other side in the opposite direction (see Fig. 2). Using now a circularly polarized x-ray beam we can probe the helicity, i.e. the sense of rotation of the cycloidal magnetic structure, by the dichroism of the left and right circular light on the magnetic Bragg peak. From the spatial map of the dichroic signal in Fig. 2 it is clear that a certain direction of the polarization corresponds clearly to the helicity of the respective cycloidal domain.

**FIG. 2:** Spatial map of the circular XRMIS dichroism measured at $(0\ T_0\ 0)$ at the Mn L-edge of a TbMnO$_3$ film of 100 nm. The sample was cooled with the X-ray beam at the "burn point" position (green ellipse approximates beam size) and measured at 11 K. The arrows indicate the electric polarization direction associated with the respective cycloidal domain.

In conclusion we have established the multiferroic order in high quality thin films of TbMnO$_3$. Through complementary measurements we prove independently the cycloidal magnetic structure and the ferroelectric polarization. We assign the formation of the multiferroic order to the very low epitaxial strains in contrast to earlier investigations of TbMnO$_3$ thin films on different substrates. More generally this exemplifies the importance of strain when incommensurate magnetic structures lead to emergent ferroelectricity.

Electrical properties and thermal stability of NdGaO$_3$/SrTiO$_3$ heterostructures with varied Ga/Nd-ratio

F. Gunkel, K. Skaja, A. Shkabko, R. Dittmann, S. Hoffmann-Eifert, and R. Waser

Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany

In the general framework of oxide electronics we investigated the structural and electrical properties of conducting NdGaO$_3$/SrTiO$_3$ (NGO/STO) heterostructures. Similar to the prominent LaAlO$_3$/SrTiO$_3$ (LAO/STO) case, these heterostructures exhibit a metallic interface between two commonly insulating oxides. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) indicate a strong growth-temperature dependence of both NGO thin-film crystallinity and stoichiometry due to the preferential evaporation of Ga-species during film growth. The observed variation of the Ga/Nd-ratio has a significant effect on the electrical properties of the NGO/STO interface. Probing the high temperature equilibrium thermodynamics of these heterostructures, we determined the dominant defect mechanism responsible for the interface conduction. Furthermore, we observe a thermal instability mediated by the loss of gallium at elevated temperatures (>1000 K) in accordance with the growth-temperature study. The results demonstrate the crucial role of Ga$^{3+}$ cations for stabilizing the interface reconstruction.

Being promising candidates for various applications in future electronics such as non-volatile memories, sensors, or transistor devices, complex oxide materials have been studied intensively within the last decades. A recent focus of research is the 2-dimensional electron system (2DEG) that can arise between polar and non-polar insulating oxides (Fig. 1 (a)). Due to their manifold physical properties, these electron systems have attracted a lot of attention. In particular, the interface between LAO and STO has been investigated intensively. The most popular model to explain the high concentration of electronic charge carriers at this interface is an electronic reconstruction resulting from the polar nature of LAO. However, crystal imperfections and defects at the interface - most prominently the presence of oxygen vacancies and the intermixing of A-site cation across the interface - can have strong impact on the interface conductivity, too. One proposed scenario is based on La$^{3+}$-ions being incorporated in the STO substrate during growth resulting in chemical donor-doping.

In foregoing studies, we have focused on the identification of the decisive defect equilibria that determine the electronic properties of the LAO/STO interface on the non-polar STO side. Resulting from this we established a general defect chemical understanding of conducting perovskite interfaces [1] that concludes a donor-type conduction mechanism [2] balanced by a complementary acceptor-type charge compensation mechanism via incorporation of Sr-vacancies [3]. Here, we report on the properties of a related conducting interface system, namely the NGO/STO interface, which allows fundamental conclusions on the role of the polar oxide side of the interface. In particular, we address the influence of the NGO cation stoichiometry on the interfacial conductivity of NGO/STO heterostructures and discuss the importance of the B-site cation, Ga$^{3+}$. We will show that the Ga-content in NGO thin films can be controlled by temperature owing to the considerably enhanced volatility of Ga-species, and that the interface conduction systematically diminishes with decreasing Ga-content.

NGO/STO heterostructures were obtained by pulsed laser deposition (PLD) of NGO on TiO$_2$-terminated (100) STO substrates (Fig. 1(a)). Films were grown at deposition temperatures between 920 K and 1070 K and at an oxygen pressure of 4x10$^{-5}$ mbar. The growth procedure was monitored by reflection high energy electron diffraction (RHEED). Subsequent to growth, structural properties and chemical composition of the NGO thin films were analyzed by XRD and XPS, respectively. Furthermore, the transport parameters of the NGO/STO interfaces were obtained from room temperature Hall measurements.

Figs. 1 (b), (c) summarize RHEED data and XRD spectra of the NGO films around the (200) peak.
data for the deposition of 20 unit cells (uc) thick NGO films grown at various deposition temperatures ($T_{\text{dep}}$). For all temperatures, RHEED intensity oscillations are observed indicating a layer-by-layer growth mode (Fig. 1(b)). However, amplitude and damping of the oscillations strongly depend on the growth temperature. For $T_{\text{dep}} = 920$ K and 970 K, clear oscillations with almost constant amplitude were observed. However, at higher deposition temperatures, the RHEED oscillations show a strong damping. Fig. 1(c) displays XRD data recorded after the growth. The main film peaks (the expected position of the (200) NGO peak is marked by the dashed line) are hardly resolved in the (0-2θ)-scans due to the small thickness of the NGO layers and interference with the (200) STO substrate peak. However, the observed thickness fringes provide information on the crystal structure of the films. They are most pronounced for the samples grown at 920K and 970K, while for the samples grown at higher $T_{\text{dep}}$, the thickness oscillations are much weaker and broadened. For the sample grown at 1070 K, thickness fringes are almost absent. However, a weak trace of a residual crystalline NGO layer is still evident. Thus, the crystal quality decreases significantly at higher deposition temperatures. Such a dependence of the growth process on temperature is not typical for PLD processes as the thin film quality should - in the first place - rather increase at higher growth temperature due to the enhanced growth kinetics.

As revealed by the analysis of the chemical composition using XPS, the decreasing crystal quality is accompanied by a dramatic change of the film stoichiometry when increasing growth temperature (Fig. 2 (a)). In particular, the Ga content in the NGO thin films decreases constantly with increasing $T_{\text{dep}}$ (Fig. 2(e)), whereas the Nd content remains unaffected. As a result, the Ga/Nd-ratio decreases constantly with increasing deposition temperature. This dramatic change can be understood by a preferential evaporation of Ga during film growth due to the enhanced volatility of Ga at elevated temperatures (see sketch in Fig. 2(f)). The same tendency of loosing gallium at elevated temperatures is known from research on gallate single crystals and ceramics as well as from III-V-semiconductor thin film research. At the highest growth temperatures the gallium deficiency is as significant as the crystallinity of the film is affected explaining the results of the XRD analysis. Figs. 2 (b)-(d) illustrate the electrical transport parameters of the hetero interfaces with varied Ga/Nd-ratio. The interfaces are conducting over a wide stoichiometry range. However, the resistance of the interfaces increases for very low Ga-contents, while both electron density and electron mobility are affected. This indicates not only an increased defect density in the non-stoichiometric interface samples but also a stoichiometry-effect on the actual reconstruction and charge compensation mechanism at the NGO/STO interface. The temperature-effect on electrical transport is enhanced for lower film thickness (red data points in Fig. 2 (b)-(d) corresponding to 8uc NGO on STO) indicating a gradual variation of stoichiometry, i.e. the Ga-deficiency is most pronounced at the surface and becomes less pronounced towards the NGO/STO interface. From the measurements, it is evident that the stoichiometry (or the Ga-content) of the NGO capping layer has crucial impact on the electrical interface properties.

In order to further test and understand the defect structure of the heterostructures, we measured the electrical conductance of the heterointerfaces in high temperature equilibrium as a function of ambient oxygen partial pressure (see Ref. [4] for more details). This measurement is dictated by equilibrium thermodynamic processes and provides fundamental information on the chemical reactions taking place at the interface. At moderate temperatures, the NGO/STO interface exhibits thermally stable metallic conduction indicating the same donor-type conduction mechanism as observed for LAO/STO in previous experiments.[2],[3] In contrast to LAO/STO, however, the interface conduction degraded, and eventually vanished above a threshold temperature of about 1000 K. Based on XRD and XPS analysis, this transition from metallic interface to insulating interface is ascribed to the full depletion of Ga during the long-term high temperature experiment – a similar but (due to a longer exposure time) more pronounced effect as observed during growth at elevated temperatures. In conclusion, we have found that a sufficient Ga-content within the NGO layer is essential not only to initialize but also to preserve the conductivity at the NGO/STO interface. This refutes a simple conduction mechanism based on the implantation of Nd$^{3+}$ donors into the STO substrate during growth. Rather, our study emphasizes the importance of the B-site cation, Ga$^{3+}$. The intact polar NGO capping layer seems to be essential for providing the driving force to generate and to stabilize the electrically conducting interface.

Thermochemical ranking and bonding nature of TeO$_2$ polymorphs

V. L. Deringer, R. P. Stoffel, and R. Dronskowski
Institute of Inorganic Chemistry, RWTH Aachen University, Germany

Ab initio modeling has become one of the methodological cornerstones for the materials-science communities. Very recently, such quantum-theoretical computations have left the “zero-Kelvin” regime and can describe materials at finite temperature, at least in principle. Here, we report such an ab initio thermochemical study of the three tellurium dioxide (TeO$_2$) polymorphs. We show that the inclusion of dispersion interactions in lattice-dynamics computations is critical to reproduce the stability ranking; this approach also affords much better predictions of the physical properties than “household” DFT does. Finally, we resolve why the three polymorphs are so close together in energy: the structures look different, but their bonding and vibrational fingerprints are nearly indistinguishable.

Quantum-theoretical simulations of solids are taking great strides to become more and more realistic, and one of the crucial steps in this regard is to predict temperature-dependent properties from theory alone. For crystalline structures with translational symmetry, one starts by computing collective lattice vibrations (phonons) and then translates them into free-energy contributions using statistical thermodynamics. This way, a self-consistent set of the precious thermochemical data can be obtained, even for metastable materials [1]. We are currently very eager to explore the possibilities of these ab initio thermochemical methods and to push their capabilities just a little further.

Thermochemical experiments offer themselves as useful benchmarks in this regard, especially when polymorphism is involved: a solid takes more than one structure, and calorimetric measurements unequivocally clarify which of them is stable at a given temperature. Complementing such experiments from the theory department, the above-mentioned tools have allowed us to follow the structural evolution of the proton conductor barium cerate [2] or the phase transition of GeO$_2$ from its low-temperature rutile type to the high-temperature α-quartz type polymorph [3]. Here, we report on another fundamental oxide compound, namely, tellurium dioxide (TeO$_2$). Together with GeO$_2$, it is a final oxidation product of tellurium-based data-storage materials, which has prompted us to start researching the atomic-scale processes leading to this oxidation damage. Besides this rather special case, when TeO$_2$ is actually an unwanted phase, the material has found widespread use due to its desirable optical properties.

FIG. 1: Crystal structures of α-TeO$_2$ and β-TeO$_2$. Van der Waals gaps in the latter are highlighted by blue shading. The recently synthesized polymorph γ-TeO$_2$ is not shown but also exhibits a three-dimensional network, like α-TeO$_2$. All figures adapted from Ref. [4] with permission. Copyright 2014, American Chemical Society.

Figure 1 outlines the well-known crystal structures of the thermodynamically stable α polymorph (dubbed paratellurite) and its β counterpart (tellurite), which was shown in calorimetric measurements to be only slightly less favorable than paratellurite; cf. a more detailed discussion in Ref. [4]. It is often argued that “household” DFT such as the generalized gradient approximation (GGA) has difficulties with layered structures; indeed, the GGA fails in reproducing the experimentally verified stability trends and predicts β-TeO$_2$ to be more stable than α-TeO$_2$ by ∆G = 2.6 kJ mol$^{-1}$ at 300 K. (A note for the expert readers: yes, the layered structure here comes out more stable than it should, but only in relative terms. This is because dispersion interactions are predominant in both polymorphs, also in the 3D networks of α-TeO$_2$.)

To amend this problem, we switched on a dispersion correction to DFT—a pairwise term added to energies and, via their gradient, to forces [5]. This way, the corrections seamlessly enter into the computation of the dynamical matrix [6] and thus into the subsequent evaluation of temperature-dependent properties. Figure 2a shows the unit-cell volumes V(T) as obtained in the quasiharmonic approximation. Uncorrected DFT predicts too large a lattice expansion, which is understandable: imagine the solid as held together by spring forces, and if some of them (namely, dispersion interactions) are unaccounted for, the lattice is predicted to expand too easily upon heating [4]. Indeed, once dispersion corrections are taken care of (bold line in Fig. 2a),
the agreement with the experimental reference value is undoubtedly better.

Including dispersion corrections not only alleviates the problems with lattice expansion—it also leads to a correct stability order, by predicting a slight preference for the $\alpha$ polymorph (0.3 kJ mol$^{-1}$ at 300 K). In Fig. 2b, we display the resulting stabilities with $\alpha$-TeO$_2$ set as the energy zero.

It is gratifying to reproduce the experimentally observed behavior but the true challenge is to understand why the compounds are so close together in energy albeit the structures look different (Fig. 1). To this end, we computed crystal orbital Hamilton population (COHP) curves, which identify bonding (stabilizing) and antibonding contributions to the band-structure energy. In all polymorphs, each tellurium is bonded to four oxygen atoms, forming two short Te–O bonds (1.88–1.95 Å) and two longer ones (2.08–2.26 Å). For both groups, COHP curves are collected by black and grey lines in Fig. 3a, respectively. This not only supports the intuitive notion of the shorter bonds being stronger (because their COHPs take more positive values), a side-by-side comparison also makes clear that the three polymorphs are extremely similar in chemical bonding.

Finally, we look back at the vibrational levels (which, according to Boltzmann statistics, are gradually filled as temperature rises). We suggest to inspect the integrated densities of phonon states (DPS), which we have evaluated in Fig. 3b. This plot corroborates the notion of similar chemical nature in the different polymorphs: especially in the low-wavenumber region, which is most readily populated, the data look almost superimposable. (They do not for GeO$_2$, which takes two polymorphs that are very different in structure and chemical nature.)

Summarizing, the three TeO$_2$ polymorphs turn out as an interesting (and challenging) test case for modern ab initio thermochemistry. With, and only with, dispersion corrections [5] to the underlying DFT computations, the stability ordering is reproduced correctly, and dispersion corrections much improve upon the computed finite-temperature materials properties [4]. The energetic similarity between the structures is reflected in their similar chemical-bonding nature.

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Ab initio calculations of the defect structure of $\beta$-Ga$_2$O$_3$

T. Zacherle$^1$, P.C. Schmidt$^2$, and M. Martin$^1$

$^1$Institute of Physical Chemistry, RWTH Aachen University, Germany
$^2$Institute of Physical Chemistry, Technical University of Darmstadt, Germany

Gallium oxide, $\beta$-Ga$_2$O$_3$, is a wide-band-gap (4.9 eV) semiconductor and has raised considerable interest due to its possible application as TCO-material [1]. In addition, amorphous, highly non-stoichiometric gallium oxide, a-GaO$_x$, exhibits unusual properties. At room temperature it shows bulk resistive switching due to mixed ionic and electronic conductivity [2], and during heating it exhibits an insulator-metal transition [3]. Nevertheless, the defect structure of $\beta$-Ga$_2$O$_3$ is still controversial.

The electrical conductivity of gallium oxide shows a $pO_2$-dependence $\sigma_{exp} \sim pO_2^{-1/4}$ [4], and the experimentally determined activation energy of the conductivity is $E_a = 1.3 - 2.1$ eV [5]. However, there is no consensus in the literature on the defect structure of the system. In particular the $pO_2$-dependence excludes the often assumed majority disorder where oxygen vacancies $V_O$ are compensated by electrons $e'$. Thus, it is the aim of this work [6] to clarify the defect structure of $\beta$-Ga$_2$O$_3$ by means of ab initio DFT-calculations using the VASP-code [7, 8].

**Formation energies** We calculate fully finite-size and band gap corrected formation energies $E_{\text{form}}$ for all possible, simple intrinsic defects according to the following formula [9] (here the example of $V_O$ is chosen):

$$E_{\text{form}}(V_O) = E^{\text{VASP}}(V_O) - E^{\text{VASP}}(\text{bulk}) + \mu_O + 2(E_F + E_{\text{VBM}}) + E_{\text{cor}}(V_O)$$

$E_{\text{cor}}$ denotes the finite-size corrections due to the periodic boundary conditions in the ab initio code, namely image-charge interactions ($E_{\text{ic}}$) [10,11] and elastic interactions ($E_{\text{el}}$) [12]:

$$E_{\text{ic}} = -\frac{aq^2}{2e_{\text{ic}}} - \frac{2aq}{3e_{\text{ic}}} + O(L_{\text{ic}}^3), \quad E_{\text{el}} \sim \frac{1}{L_{\text{ic}}}$$

We correct for the image-charge interactions with a method proposed by Freysoldt et al. [11]. For GGA-energies we perform calculations for different sizes of the supercell (different supercell length $L_{sc}$, see Fig. 1). Therefore, we get also the elastic finite-size-scaling. For band gap corrected hybrid functional HSE06-energies we only correct for the image charges and take the GGA-energy-correction for the elastic effects.

**FIG. 1:** Finite-size scaling of formation energies for differently charged cation vacancies $V_{\text{Ga}^\pm}$. The extrapolated value for infinite dilution of the defect corresponds to the intersection of the fitting lines with the energy axis. Similar results are obtained for vacancies $V_{\text{Ga}^\pm}$ occupying the second gallium position within the monoclinic structure of $\beta$-Ga$_2$O$_3$.

The resulting formation energies are plotted against the Fermi-level (see Fig. 2). Oxygen vacancies have low formation energies for low $pO_2$, gallium vacancies are important for high $pO_2$ and high Fermi-levels (corresponds to donor-doping).

**FIG. 2:** Formation energies of the different intrinsic defects plotted against the Fermi-level (RHS: high $pO_2$, LHS: low $pO_2$; the vertical line at $E_{\text{Fermi}} = 4.7$ eV shows the position of the CBM).
Defect concentrations Assuming dilute defects, concentrations can be calculated using the formation energies and imposing charge neutrality. For the intrinsic case we obtain for the electron concentration the wrong $pO_2$-dependence with an exponent $-1/6$. Only if we assume slight donor doping (10 ppm) we obtain the experimentally found $pO_2$-dependence, but only for relatively high $pO_2$. Then negatively charged gallium vacancies compensate the donor.

To improve the results free energies were computed for gallium vacancy formation. From the phonon frequencies (see Fig. 3a) the formation entropy $S_{\text{form}}$ and the formation free energy $F_{\text{form}} = E_{\text{form}} - T S_{\text{form}}$ (see Fig. 3b) are obtained.

FIG. 3a: Phonon-dispersion of a defective supercell containing a cation vacancy $V_{\text{Ga}}''''$.

FIG. 3b: Entropy of formation for a cation vacancy $V_{\text{Ga}}''''$. ($V = \text{const}$ and $p = \text{const} = 0$) and contribution $-TS_{\text{form}}$ to the free energy of formation.

With inclusion of entropic effects the experimental behavior can be reproduced. We get a $pO_2$-dependence for the electron concentration with exponent $-1/4$ over the whole stability range of $pO_2$ (see Fig. 4). We also get an activation energy of the conductivity of $E_a = 1.7$ eV.

FIG. 4: Calculated defect concentrations assuming weak donor doping (10 ppm) for $T = 1273$ K. We get the experimentally observed $pO_2$-dependence for the electron concentration, while gallium vacancies compensate the donor.

Conclusions We calculated fully finite-size and band gap corrected formation energies for intrinsic defects in β-Ga2O3 [6]. We can reproduce both the experimental $pO_2$-dependence and the experimentally measured activation energy of the conductivity, $\sigma \sim pO_2^{-1/4}$, $E_a = 1.7$ eV ($E_a^{\text{exp}} = 1.3$ – 2.1 eV). The absolute values of $\sigma$ also agree well with experiment. In our proposed defect model donors are compensated by cation vacancies $[D\cdot] = 3[V_{\text{Ga}}''']$ while electrons are only minority defects. Entropic contributions $-TS_{\text{form}}$ are crucial to explain the experimental behavior.

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Networks of ABA and ABC stacked graphene on mica observed by STM

S. Hattendorf, A. Georgi, M. Liebmann, and M. Morgenstern
II. Physikalisches Institut B, RWTH Aachen University, Germany

Graphene flakes are prepared on mica by exfoliation and studied by scanning tunneling microscopy (STM). On few-layer graphene, a triangular network of partial dislocations separating ABC stacked and ABA stacked graphene was found similar to the networks occasionally visible on HOPG. We found differences in the electronic structure of ABC and ABA stacked areas by scanning tunneling spectroscopy, i.e., a pronounced peak at 0.25eV above the Fermi level exclusively in the ABA areas, which is responsible for the different apparent heights observed in STM images.

Since Geim and Novoselov produced monolayer graphene flakes by exfoliation [1], graphene developed into a favorite research topic. Recently, trilayer graphene came into focus [2]. For more than two layers, graphene can be stacked either in an ABA or in an ABC sequence. Networks of partial dislocations connecting triangular ABA and ABC areas have been observed in HOPG by electron microscopy [3] and by STM revealing an apparent height contrast between differently stacked areas [4,5]. The stacking order influences the electrical properties. It was predicted that an electric field $E$ can open a band gap of up to 200 meV for ABC stacking, but not for the ABA stacking [6,7]. Thicker ABC layers exhibit conducting surface states in the absence of $E$, but an insulating bulk, similar to weak topological insulators [7].

We show a network of ABA and ABC stacked areas with sizes down to $(200\text{nm})^2$ on graphene on mica, similar to on HOPG [4,5]. We identify a peak at 200meV by scanning tunneling spectroscopy, which is only visible in the ABA stacked region and turns out to be responsible for the different apparent heights in STM images. This peak makes the distinction of the different stackings possible.

The STM measurements were carried out at 300 K in a home-built UHV system using tungsten tips.

Figure 1 shows an optical image of the prepared sample with the corresponding Raman spectra for one and two layers [9]. Only this sample (one of three) exhibited the triangular pattern within the area labeled ‘6L’. This height was determined by AFM by comparing the height of adjacent regions.

STM images of the six-layer graphene area, shown optically in Fig. 1 (a), are shown in Fig. 2 reveal an area with a triangular pattern. Triangles pointing in different directions exhibit apparent heights differing by 1-4Å. Due to the similarity to the patterns found previously on HOPG [3-5], we assign them to a partial dislocation network separating triangular areas of ABA and ABC stacked graphene. Figure 2 (a) and (b) show two large-scale images, which have been measured subsequently on the same area with different voltage polarity; white circles mark a defect, i.e. the same position in both images; notice the contrast inversion between (c) and (d).

Graphene samples were prepared by exfoliation [1] on freshly cleaved muscovite mica in a dry air box and contacted by indium micro-soldering[8].

FIG. 1: (a) Optical image of the sample recorded with polarization microscopy; layer thickness n in monolayers of graphene is marked as nL. (b) Corresponding Raman spectra of the mono- and bilayer regions.

FIG. 2: STM images of partial dislocation network on few-layer (6 ± 1 layers) area of graphene on mica. (a), (b) are recorded on the same area with 2 hours in between; $V = 0.4V$, $I = 0.1nA$, scan speed: 2μm/s; white circles highlight a defect marking the same area in (a) and (b); a line defect is indicated in both images; notice the change of the network towards a more regular structure from (a) to (b); (c), (d) are recorded subsequently on the same area with different voltage polarity; white circles mark a defect, i.e. the same position in both images; (c) $V = 0.3V$; (d) $V = -0.3V$; $I = 0.15nA$; 1μm/s; notice the contrast inversion between (c) and (d).
largely symmetric with respect to ED. We checked that the appearance of such a relaxed structure does not depend on scan direction, which, however, does not exclude that the depinning was initiated by the scanning process. The large scale mobility of the network underlines that the apparent height is not caused by a topographic feature.

The triangles with convex edges were assigned to the energetically more favorable ABA stacked area. The contrast between ABA and ABC stacked areas inverts with bias polarity (Fig. 2(d) and (e)). Also, the contrast could be inverted by voltage pulses changing the tip. These observations strongly suggest that the observed contrast is not of topographic but of an electronic origin.

![Graph](image)

**FIG. 3:** dI/dV spectra acquired on ABA stacked (solid) and ABC stacked (dashed) regions. Spectra of the same color were acquired on adjacent regions directly after each other. The black, red and blue measurements are stabilized at V = 1 V and I = 0.2 nA, V_{mod}=40 meV, the pink ones at V = 0.5 V and I = 0.2 nA, V_{mod}=20 meV. Measurements are shifted vertically for clarity. Vertical lines mark minima.

To analyze the electronic differences, dI/dV spectra, which are proportional to the local density of states (LDOS), were acquired on ABC and ABA areas as shown in Fig. 3. The spectra exhibit several minima marked by vertical lines and a peak at V = 0.25 V only on the ABA areas. Since the curves were acquired alternately on ABA and ABC stacked areas, one can exclude that the spectroscopic differences are caused by a tip change. The global minimum is found around 0 mV for ABA areas and at 125 mV for ABC areas indicating a relative offset of the Dirac point energy E_D. The peaks and dips are slightly moved upwards by about 20 mV in the spectra acquired at smaller tip-surface distance (pink curves). This indicates an upwards band bending at the graphene surface induced by the work function mismatch between tip and graphene and implies an electric field penetration into the graphene sample [11]. No band gap is observed neither on the ABA nor on the ABC areas, which means that a band gap, if present, is smaller than about 100 meV being the energy resolution of the experiment [11]. Theoretical calculations [7] of ABA and ABC stacked graphene find complex band structures changing with electric field, which, however, are largely symmetric with respect to E_D. We checked that they cannot explain a single peak at +0.25 eV, which is only found in ABA areas, using reasonable assumptions for the electric field penetration, which itself depends on tip-sample distance and screening. Since the peak is observed close to the tentative E_D of the ABC area, i.e. where a gap exists in the bulk of the ABC stacked areas, it might indicate a confinement of electronic states within the ABA areas (see below).

The question is, of course: what causes the differences in LDOS, respectively the LDOS peaks? Mechanical differences were excluded, due to height differences between ABA and ABC areas not depending on the tip-sample distance. A Fabry-Perot type interference, similar to a proposal by Kobayashi et al. [5], was considered. The idea is the following: electrons tunneling into the graphene multi-layer are reflected back at the interface between graphene and mica forming an interference pattern with the incoming electrons. Depending on the energy of the electrons, this interference can be constructive or destructive causing peaks and minima in the LDOS. The energy of these peaks is calculated using the energy dispersion of graphite orthogonal to the surface [5]. The stacking fault might scatter the electrons isotropically due to the band gap in its interior prohibiting the vertical interference, and, thus, explaining the absence of strong peaks in the ABC region. However, for the determined layer thickness N = 6, the four lowest energy peaks would be at about -0.7 eV, -0.35 eV, +0.2 eV, +0.9 eV with respect to E_D. This is in disagreement with the measured spectra exhibiting a single strong peak at about 0.25 eV and a smaller one at 0.4 eV, but no strong peak around -0.35 eV. Thus, such a model cannot explain the observed dI/dV curves straightforwardly. We propose tentatively that an additional lateral confinement by the gap within the interior of the ABC area strengthens the vertical Fabry-Perot resonance in the ABA region which is closest to E_D, i.e. the one at 0.2 eV. Thus, the ABA area surrounded by forbidden areas for the electrons at 0.2 eV acts as a cavity for the electron waves. But more work is required to substantiate such a hypothesis. Notice finally that the network of stacking faults could be, in principle, transformed into a triangular network of 200 nm quantum dots by applying a gate voltage to open the band gap in the ABC regions [6,7].

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Parallel carbon nanotube quantum dots and their interactions

K. Goss, C. M. Schneider, and C. Meyer
Peter Grünberg Institut-6, Forschungszentrum Jülich, Germany

It is our goal to gain a fundamental and comprehensive understanding about the influences of molecular interactions on electronic transport in low-dimensional systems. Here, we demonstrate low-temperature transport through carbon nanotube quantum dots coupled in parallel. By tuning the system to different states, we use quantum transport as a spectroscopic tool to investigate the interdot coupling and show a route to distinguish among the parallel dots. We identify conditions for the tunneling rates in the system that are required in order to observe different manifestations of the interdot coupling in the transport spectra.

Carbon nanotubes (CNTs) are a versatile material for electronics. They possess extraordinary electronic and thermal transport properties, while at the same time being mechanically flexible and strong. The current is carried by the π-orbitals of the macromolecule. Thus, the electronic transport can be strongly influenced by the environment; in particular by chemical functionalization of individual CNTs to create new hybrid nanodevices such as spin valves [1]. The interactions involved in such a functionalization are not yet fully understood but are expected to also play an important role in the transport properties of other interacting π-systems such as graphene or individual molecules. Much effort has been put into studying quantized transport in these systems. In contrast to graphene and individual molecules, quantum transport on clean, individual CNTs today is well established. Therefore, it can be used as a spectroscopic tool to investigate more complex devices. Within this context, CNTs bundled together in the form of a rope represent a generic and readily available system to study the electrical transport of interacting molecules.

Tip-enhanced Raman scattering revealed that the device we investigate consists of a bundle of seven CNTs with diameters between 0.6 and 1.3 nm in the quantum dot region [2]. The resistance at room temperature is 290 kΩ with a linear current-voltage characteristic indicating a metallic character. Low-temperature transport measurements are performed in a dilution refrigerator at a base temperature of ~ 30 mK.

The Coulomb diamonds in Fig. 1 originate from one quantum dot (QD), which we label as the main dot, and the secondary resonances marked by arrows originate from side dots formed in parallel CNTs within the rope [3]. These secondary resonances are part of a Coulomb diamond pattern with smaller slopes of the diamond edges due to a weaker backgate coupling $\alpha_{gt}$ of the side dots.

Three main signatures are used to discriminate the parallel quantum dots [4]. First, anticrossings caused by a tunnel coupling $t$ between quantum dot states on different dots can be observed at meeting points between resonance lines. Second, a capacitive coupling characterized by the capacitance $C_{ms}$ between the dots leads to a voltage shift $\Delta V(i)$ in the secondary resonances when proceeding from one Coulomb diamond to the next.

Third, the bias coupling $\alpha_{sc}, \alpha_{dr}$, which is due to the interaction of the QDs with the leads, can be deduced from the slopes of the diamond edges in the stability diagram. These are represented by the slopes of the arrows indicating the secondary resonances in Fig. 1. Sweeping the gate voltage between -2.3 V and 1.1 V we find signatures of in total six side dots. Their coupling parameters are listed in table I. Thus, transport measurements and Raman scattering show the same number of CNTs.

Fig. 2 presents several charge states of the main dot at $B = 10$ T. Comparing the secondary resonances of side dot 5 in Fig. 2 with those in Fig. 1, two differences can be observed in the single electron tunneling (SET) region of the main dot. First, excited states of this side dot are visible,
which cause parallel secondary resonances with equal coupling and interaction parameters.

| QD | $\alpha_{gt}$ | $\alpha_{sc}$ | $\alpha_{dr}$ | $|t|$(meV) | $\Delta V_i$(meV) |
|----|---------------|---------------|---------------|-------------|----------------|
| main dot | 0.05 | 0.36 | 0.59 | 0 | 0 |
| side dot 1 | 0.001 | 0.001 | 0.997 | 0 | 0 |
| side dot 2 | 0.007 | 0.007 | 0.919 | 0 | 0.225 |
| side dot 3 | 0.001 | 0.001 | 0.997 | ≠0 | 0.075 |
| side dot 4 | 0.006 | 0.006 | 0.955 | ≠0 | 0.150 |
| side dot 5 | 0.007 | 0.007 | 0.919 | 0.075 | 0.200 |
| side dot 6 | 0.019 | 0.019 | 0.216 | ≠0 | 0.100 | 0.400 |

Table I: Coupling parameters and interaction properties of the observed QDs.

Second, the voltage shift $\Delta V(5)$ of the secondary resonance is found to occur within the SET regime [see arrow in Fig. 2] and not at the edge of the subsequent Coulomb diamond (compare inset sketches). This effect is best visible for the secondary resonance with the lowest energy and has its origin in the relative tunneling rates of the main dot and the side dots; an electron resides for a long time on the main dot state within the bias window due to a reduced tunneling rate towards the drain electrode. In Fig. 2, the conductance via the main dot is very low (faint Coulomb diamonds), indicating such a reduced tunneling rate of this QD.

FIG. 2: Differential conductance plot with a magnetic field $B = 10$ T. Main dot Coulomb diamonds are indicated in red. Secondary resonances of side dot 5 are indicated by black lines. The shift $\Delta V(5)$ of one resonance is indicated by the arrow. The inset shows the two ways in which a shift due to capacitive coupling with the main dot can appear.

A similar effect with the same physical origin can be observed in Fig. 3, which shows another transport measurement at $B = 0$ T at similar charge states as in Fig. 1. The position of the secondary resonance from side dot 5 is difficult to recognize due to a low conductance in this particular measurement. Instead, a shift of the diamond edge $\Delta V(m)$ can be observed close to the meeting point of the secondary resonance with the main resonance. This is, like the voltage shift

FIG. 3: Differential conductance plot exhibiting a main resonance shifted by $\Delta V(m)$. (see black arrows and inset). The secondary resonances of side dot 5 and 6 are indicated in yellow.

in the secondary resonances, a manifestation of the capacitive coupling between the main dot and side dot 5. In a system of capacitively coupled quantum dots, the chemical potential of the quantum dots will mutually depend on each other. Hence, resonance lines of any dot— not only a side dot—are expected to shift when the number of electrons on the parallel quantum dot is changed. This means that also a situation inverse to what we have discussed so far can appear in the stability diagram. Such a situation involves the tunneling of an additional electron via a side dot state, which changes the potential for the electrons on the main dot. Then, a shifted main dot diamond edge is expected at energies higher than the respective secondary resonance, i.e., in the SET regime of the side dot as observed in Fig. 3.

The exact position and appearance of a shift in the SET regime of parallel QDs depends thus on their relative tunneling rates. Our results provide the basis to understand quantum transport via parallel quantum dots—a important issue in molecular transport where a large variety of hybrid transport devices with new functionalities are expected.

Electronic and magnetic properties of graphene nanoribbons on Au(111)

Y. Li1,2, W. Zhang1, M. Morgenstern3, and R. Mazzarello1

1 Institute for Theoretical Solid State Physics, RWTH Aachen University, Germany
2 Institut für Energie- und Klimaforschung-6, Forschungszentrum Jülich, Germany
3 II. Institute of Physics B, RWTH Aachen University, Germany

One-dimensional graphene nanoribbons with zigzag termination have attracted considerable interest recently. Mean-field calculations indicate that these systems possess magnetic electronic states localized at the edge, with antiferromagnetic coupling across the edge [1]. This property could lead to possible applications in the field of spintronics [2]. Although most sophisticated calculations have challenged this picture yielding a singlet ground-state [3], the magnetic properties of these systems remain of great interest and experimental efforts to detect edge magnetism are still intensive. Recently, scanning tunneling microscopy experiments performed by Tao et al. [4] have provided convincing evidence for the presence of edge states in zigzag ribbons prepared from carbon nanotubes by chemical unzipping and deposited on Au(111). A peak or a double-peak close to the Fermi energy EF was observed in the local density of states close to the edge, with a peak splitting scaling inversely with the width of the nanoribbon. Here we report on a density functional theory study of realistic models of zigzag nanoribbons on Au(111) [5], which aims at better understanding these experimental findings.

We start our analysis discussing the non-passivated model with zero chiral angle. Due to the strong chemical interaction at the edge, the nanoribbon bends considerably: the distance between C atoms and Au(111) is much larger in the interior of the ribbon than at the edge (Fig. 1(a)). Due to the lattice mismatch, a small corrugation of about 0.17 Å occurs. As a result, some edge C atoms (4 out of 7) are in a quasi on-top configuration. The remaining edge atoms are in a quasi hollow or bridge configuration.

Figure 1: (a) Side view of the relaxed model of the H-free graphene nanoribbon on Au(111). (b) Projected density of states (PDOS) onto the p orbitals of an edge C atom at on-top site (denoted as C1t) and at hollow site (C1h), and PDOS of the d states of the respective nearest neighbor Au atoms (denoted as Au5 and Au6). The plots of a charge isosurface of a σ* state contributing to the peak at −0.2 eV below EF (EF corresponds to the zero of the energy) and of a π state contributing to the peak at 0.3 eV above EF are also shown.

After relaxation, this models turns out to be non-magnetic. To understand this finding, it is useful to analyze the electronic structure at the edge. The projected density of states (PDOS) onto the p orbitals of the edge C atom at on-top site and hollow site display two main peaks near EF (Fig. 1(b)). In the case of the C atom at the on-top site, the two peaks are at −0.2 eV below EF and 0.3 eV above EF, respectively. The peaks in the PDOS of the nearest neighbor Au 5d orbitals clearly indicate that a strong hybridization between the latter states and the C 2p orbitals occurs. More specifically, a pronounced peak in the Au d PDOS...
driven geometrical relaxation at the edges \[7,8\]. In the hollow case, two peaks are observed in the PDOS of the C \(p\) states and Au \(d\) states near \(E_F\) as well. In Fig. 1(b), we also plot the charge isosurface of two states contributing to the first and second peak in the PDOS of the C \(2p\) orbitals, respectively. The different shape of the charge distribution indicates that the two states have a different nature: the peak above \(E_F\) is due to the edge state of the nanoribbon, whereas the one below \(E_F\) is due to states originating from \(\sigma\) bonding between C and Au atoms. A more thorough inspection shows that the latter peak corresponds to antibonding \(\pi\)-\(d\) states, whereas the corresponding bonding states have much lower energies of the order of 5 eV below \(E_F\) \[5\]. In the on-top case, the 5\(d_{\sigma}\) and 5\(d_{\pi}\) orbitals of the Au contribute to the bonding with the C \(2p\) states; in the hollow case, 5\(d_x\) orbitals contribute significantly too. Au 6\(s\) and 6\(p\) orbitals play a minor role in this bonding. Since the antibonding \(\sigma\) states have lower energies than the edge states, the latter states are mostly unoccupied and no edge magnetism can occur.

We have also performed self-consistent calculations of the ground state of this model including a) spin-orbit coupling and b) a Hubbard U correction of 1.5 eV for the \(d\) states to improve the agreement between experimental and theoretical energies of the gold surface states with \(d\) character. It turns out that these additional ingredients do not change the magnetic properties of this system. Similar results hold for the model of the nanoribbon with \(\theta=5^\circ\).

Notice that electronic properties of nanoribbons on Au(111) are very different from those of ribbons deposited on Ir(111). In the latter case, there are no localized states at the edges, irrespective of whether the nanoribbon is passivated with H or not. This property is due to the interplay between a strong and intricate hybridization of the graphene \(\pi\) orbitals with Ir \(d\) orbitals and a lattice-mismatch driven geometrical relaxation at the edges \[7,8\].

Next, we consider the H-terminated model. In this case, the interaction between the nanoribbon and the surface is very weak and the ribbon is only slightly bent (Fig. 2(a)). The ribbon is magnetic with a magnetization comparable to that of a free-standing ribbon. The spin-polarized PDOS of the \(2p_z\) orbitals of an edge C atom are shown in Fig. 2(b). The splitting between spin majority and minority \(2p_z\) peaks on an edge is about 0.7 eV.

Since the edges of the nanoribbons considered in Ref. \[4\] display a large edge curvature, they resemble the H-free model of Fig. 1. However, a comparison of the experimentally observed peak splitting with the calculated one is difficult. In that the experimental widths of the ribbons vary between 8 to 20 nm and are thus much larger than in our models. The experimental splitting ranges from 50 to 20 meV \[4\] and is an order of magnitude lower than the one we obtained. Therefore, it is not possible to assign directly the calculated splitting to the experimental results. Nevertheless, our study clearly indicates that it is questionable to interpret a double peak around \(E_F\) alone as a sign for edge magnetism.

In conclusion, we have shown that zigzag graphene nanoribbons deposited on Au(111) possess edge states. However, H-free nanoribbons do not exhibit a significant magnetization at the edge, due to the strong chemical bonding between the edge C atoms and Au atoms. On the contrary, H-terminated ribbons interact very weakly with the substrate, and thus display magnetic properties similar to those of free-standing nanoribbons.


We report on pulsed-gate transient current spectroscopy and relaxation time measurements of excited states in graphene quantum dots (QDs). We have fabricated and characterized a QD device coupled to highly sensitive nearby charge sensors. The advanced device design allows tuning the tunneling barriers down to the low MHz regime, while monitoring their asymmetry. Applying a RF pulse scheme we measure transient currents through electronic excited states and we can estimate a lower bound for charge relaxation times on the order of 60-100 ns.

Graphene quantum dots (QDs) are attractive candidates for solid-state quantum bits. Weak spin-orbit and hyperfine interaction promise spin qubits with long coherence times. Over the past years, graphene QDs have been studied intensively and e.g. excitation spectrum, spin-filling sequence, and electron-hole crossover have been investigated. However, their relaxation dynamics have remained widely unexplored. This is mainly due to challenges in device fabrication, in particular concerning the control of carrier confinement and the tunability of the tunneling barriers, both crucial to experimentally investigate decoherence times.

The investigated devices [1,2] are based on single layer graphene flakes obtained by mechanical exfoliation from bulk graphite. Flakes are transferred to Si/SiO₂ substrates. Raman spectroscopy is used to identify single-layer flakes. The graphene nanostructures are defined by electron beam lithography (EBL) and reactive ion etching (Ar/O₂ plasma). Metal contacts are fabricated by an additional EBL step and lift-off.

The QD is connected to the source and drain leads via long and narrow constrictions acting as tunneling barriers (see Fig. 1a). The two graphene nanoribbons in close vicinity to the QD are used as highly sensitive charge detectors (CDs) and to tune the tunneling rates of the barriers down to the low MHz regime. Two additional gates control the electrochemical potential of the QD. A bias-tee mixes AC and DC signals.

The back gate tunes the overall Fermi level. In the regime of low charge carrier density the device is characterized by low-bias transport. By means of the nanoribbons the tunneling barriers can be tuned such that the dot transmission rate measures below 1.25 MHz. All measurements are performed in a dilution refrigerator with an electron temperature around 100 mK.

Fig. 1b shows a measurement of the current through the QD (I₂D) as a function of the central gate voltage (VCG) in a regime where transport is dominated by Coulomb blockade. The simultaneously measured current through the charge detector (I₂D) features sharp steps coinciding with the Coulomb peaks. The detector is even sensitive to charging events on the QD where the direct current through the QD is below the detection limit of about 50 fA.
small which is essential for pulsed-gate spectroscopy.

FIG. 2: Finite bias spectroscopy. (a) Current through the quantum dot as function of the gate voltage $V_{CG}$ and the bias $V_{SD}$. Dashed lines are a guide to the eye. (b) Differential conductance of the QD, $dI_{QD}/dV_{SD}$. Excited state resonances can be clearly seen (see arrows). (c) Derivative of the charge-detector current $I_{CD}$ with respect to $V_{CG}$. Regions of high $dI_{CD}/dV_{CG}$ correspond to the onset of the transitions with the largest rate, thus providing information on the asymmetry of the tunneling barriers. This effect can be bias dependent and can change from state to state.

The relaxation dynamics of the QD is addressed by transient current spectroscopy. The averaged DC current is recorded as function of a square voltage pulse applied to the central gate. The pulse rise time has to be faster than the tunneling rates and thus the transmission through the barriers has to be tuned down sufficiently. At low frequencies (e.g., 100 kHz, Fig. 3a) the Coulomb resonance splits into two distinct peaks while at high frequencies (e.g., 18 MHz, Fig. 3b) additional lines originating from transport through excited states appear. The level spacing determined by this technique is in good agreement with the one extracted from DC finite-bias spectroscopy (compare panels in Fig. 3b).

The QD levels are pushed out of the bias-window in the first half of the pulse such that they get depopulated (see Fig. 3c). In the second half only the excited state is positioned in the transport window and thus electrons can tunnel through the QD via this excited state. If the ground state gets filled (by tunneling from the leads or by relaxation from the excited state) transport is blocked until the next pulse cycle initializes the system again. An average DC current can be measured at frequencies faster than the blocking processes. Thus an upper bound for the relaxation rate can be estimated.

A pulse scheme introduced by Fujisawa et al. [3] with varying pulse length $T_A$ and fixed amplitude and $T_B$ allows more precise determination of the relaxation rate. Measuring the DC current as a function of the pulse length $T_A$ the average number of electrons $<n>$ tunneling through the device per pulse cycle can be determined. Fig. 3d compares $<n>$ considering tunneling only via ground state transitions (blue) and via excited state transitions (red). In the first case a linear dependence can be observed whereas in the latter $<n>$ tends to saturate. Fitting the data according to $n(T_A) = n_{sat} [1 - \exp(-\gamma T_A)]$ with $n_{sat}$ the saturation value for long $T_A$, yields an estimate on the rate of the blocking processes $\gamma = 12.8 \text{ MHz}$. Transport can be blocked by relaxation and by tunneling from the leads. Thus $\gamma$ is approximately the sum of the tunneling rate $\Gamma$ and the invers of the relaxation time $\tau$. By pulsed gate spectroscopy measurements in different regimes a lower bound for the relaxation time of 60 - 100 ns can be given.

These times are by a factor of 5-10 larger compared III/V QDs which can possibly be explained by a reduced electron-phonon interaction in graphene due to the absence of piezoelectric phonons. A rough estimate for relaxation time of 40-400 ns can be obtained considering the coupling to longitudinal acoustic phonons via the deformation potential as the dominant relaxation mechanism.

In summary, we have studied a highly tunable graphene quantum dot by DC finite-bias spectroscopy and by pulsed-gate transient current spectroscopy. By this technique a lower bound for the charge relaxation time of 100-600 ns could be estimated.

Half Metal in Graphene Multilayers

J. Yuan and C. Honerkamp
Institute for Theoretical Solid-State Physics, RWTH-Aachen University, Germany

Charge neutral bilayer graphene has a possible gapped ground state as transport experiments demonstrate. One of the plausible ground states is a layered antiferromagnetic spin density wave (LAF) state. We propose that lightly charged bi-layer graphene in an electric field perpendicular to the graphene plane may be a half metal as a consequence of the inversion and particle-hole symmetry broken in the LAF state. We show this explicitly by using a mean field theory on a bilayer Hubbard model for the bilayer graphene. We provide a possible way to design half-metals from correlated systems. We also extend our results to ABC trilayer graphene.

In the single-electron picture bilayer graphene (BLG) is a gapless semiconductor with parabolic valence and conduction bands touching at the high-symmetry points K and K'. This state is unstable in the presence of electron-electron interactions. Experimentally, there are many evidences that the BLG at charge neutrality may be a half metal as a consequence of the spin density wave. There are many unstable in the presence of electron-electron field increases and to close at a field 15 mV·nm−1.

\[ H = H_0 + H_U + H_p \]  (1)

where \( H_0 = H_{\text{intra}} + H_{\text{inter}} \) is the kinetic energy part, \( H_U \) is the on-site Coulomb interaction, and \( H_p \) describes the electric potential due to the applied electric field. The intra-layer hopping is given by

\[ H_{\text{intra}} = -\gamma_0 \sum_{i(j)} \sigma [a^\dagger_i \sigma (b_i \sigma (j) + H.c.) - \mu \sum_{i} n_{i \sigma} (i)] \]  (2)

Here \( a_i \sigma \) (\( b_i \sigma \)) are the electron annihilation operator on sublattice A(B), and \( l = 1,2 \) for the bottom and top layers as illustrated in Fig. 1. \( \sigma \) is the spin and site, respectively. \( \gamma \) sums over all nearest neighbor sites. Here, we only consider the nearest neighbor hopping for simplicity and expect the small remote hopping will not change the basic physics. \( \mu \) is the chemical potential. We consider an interlayer hopping between two sites \( i \) and \( i' \) on top to each other,

\[ H_{\text{inter}} = \gamma_1 \sum_{ii'} \left[ b^\dagger_{i \sigma} (i) a_{2 \sigma} (i') + H.c. \right]. \]  (3)

The Hubbard U term is given by

\[ H_U = U \sum_{i} n_{i \sigma} (i) n_{i \sigma} (i). \]  (4)

The effect of the external electric field is modeled by an electric potential \( V \) between two layers,

\[ H_p = \sum_{i} n_{i \sigma} (i) \rho_{i \sigma} (i), \]  (5)

with \( V = -e d_0 E \), and \( E \) is related to \( E_\phi \) as below. Let \( E \) be the electric field between the two layers, then we have \( V = (i-j) V_\phi \), and \( E \) is related to \( E_\phi \) by \( E = E_\phi - 2\pi e (\rho_i - \rho_j) \), where the electron density in layer \( l \) is given by \( \rho_{i \sigma} (i) = \sum_{i} n_{i \sigma} (i) / S \), with \( S \) the area of each layer. And we also use \( d_0 = 0.334 \) nm and \( 2\pi e^2 d_0 \approx 3 \times 10^{-11} \) meV·cm².

At \( E_\phi = 0 \), our theory gives a gapped LAF ground state at half filling, consistent with the experiment, and with previous theoretical works by using functional renormalization group theory [2]. In the LAF state, the charge distribution is uniform and the spins are anti-parallel to each other. There is a two-fold degeneracy for the spin configurations, related to the time reversal. The net spin polarizations in the top and bottom layers have an opposite sign, and their sum gives a null magnetization. For \( U = 6.64 \) eV, we have a gap of
\( \epsilon_g \approx 2 \text{ meV} \), approximately the gap in the BLG measured in the experiment.

We proceed to discuss the effect of the electric field to the half filled BLG. At half filling, an electric field breaks inversion symmetry \( \mathcal{I} \). As \( V' \) increases, the spin-down excitation gap increases and the spin-up excitation gap becomes narrowed. At a critical value \( V' = V_c = 1.8 \text{mV} \), there is a first order transition from the LAF state to the spin symmetric normal state. There is a sudden change of the gap at \( V_c \). At \( V' > V_c \), the gap increases monotonously with \( V' \). There is a charge transfer from sublattice A in layer 1 to sublattice B in layer 2, and a smaller amount of charge transfer from sublattice B in layer 1 to sublattice A in layer 2 (inter-layer nearest neighboring sites). We remark that \( V_c \approx 1.8 \text{mV} \) corresponds to an applied electric field \( E_0 \approx 15 \text{mV} \cdot \text{nm}^{-1} (\epsilon \approx 1.0) \). This is in good agreement with the external electric field at the phase transition point estimated in the transport measurement.

![Figure 2](image.png)

**FIG. 2:** (a) Energy bands of the BLG in an interlayer electric potential \( V' = 1.4 \text{mV} \) of a doped graphene with electron density \( \delta n = 2 \times 10^{10} \text{cm}^{-2} \). Solid lines are for spin-up and dashed lines for spin-down. (b) Schematics of probing magnetization by using torque magnetometry experiment.

The most interesting case is at \( \mu > 0 \) but small, where we make a metallic state in the background of LAF. Away from half filling, there is no particle-hole symmetry, and the spin structure of the LAF state breaks \( T \otimes \mathcal{I} \) symmetry. It gives a half metal with a net magnetization. Experimentally, the shift of the chemical potential can be realized by tuning the gate voltages, which can be controlled independently together with the tuning of the electric field in double gated BLG device. In Fig. 3(a), we plot the low energy bands for the BLG at the lightly charge density \( \delta n = 2 \times 10^{10} \text{cm}^{-2} \). This is equivalent to \( 2.5 \times 10^{-6} \) electrons per carbon site on the BLG. As we can see from the figure, the spin-up conduction band is partially filled but the spin-down conduction band is completely empty. The system is a half metal with a full spin polarization in its carriers. The electric field induces time reversal symmetry broken in this case. The surface magnetization per area is \( M = \delta n \times \mu_B \times 2 \times 10^{-4} \mu_B / \text{nm}^2 \), with \( \mu_B \) the magnetic moment of graphene atom, and \( \mu_B \) the Bohr magneton and \( \mu_B \) the Lande \( g \)-factor for the graphene, which is about 2-2.5. The magnetization is tiny, but possibly detectable by using torque magnetometry experiment, as schematically illustrated in Fig. 3(b). In quantum spin Hall state, the two valleys picks an opposite spin flavor, the system will have zero magnetization even when it is doped, as protected by time-reversal symmetry.

We also extend our studies to trilayer graphene. It is reported quite recently that ABC trilayer graphene in experiment has a giant spontaneous gap about 40meV [4]. According to the data, the LAF is also very probable to be the ground state, supported by theory [5,6]. By adding top and bottom gates, we are able to break the inversion symmetry of the trilayer. In LAF state, this will cause a spin splitting in the band structure. Upon doping, we can again have a magnetized half-metal state.

![Figure 3](image.png)

**FIG. 3:** The band structure of the doped TLG with a perpendicular field \( V' = 0.028V \). The green dashed line is the chemical potential. The red dashed line gives the band structure of the spin up electrons around \( K' \); while the blue solid line is the band structure for the spin down electrons.

Because of existence of a giant spontaneous gap in trilayer, \( E \)-field and doping can be varied in a much wider range, and also the gap for minority electrons is about 10eV. This may provide a way for achieving the half-metal state at much higher temperatures.


Magnetic Correlations in Short and Narrow Graphene Armchair Nanoribbons

M. Golor, C. Koop, Th. C. Lang, S. Wessel, and M. J. Schmidt
Institut für Theoretische Festkörperphysik, RWTH Aachen University, Germany

Motivated by the recent successful bottom-up synthesis of high-quality graphene nanoribbons with armchair edges and perfect zigzag ends [1,2], we consider magnetic correlation effects in these systems. We find that those nanoribbons enable the investigation of the basic building blocks of the much-studied but still elusive phenomenon of edge magnetism [3]. Indeed, there are localized electronic states at the zigzag ends of the studied armchair ribbons. These correspond to the usual extended edge states in the context of edge magnetism. As the short and narrow armchair nanoribbons are experimentally and theoretically well controlled, they constitute a convenient model system for the study of the fundamentals of edge magnetism. Two experiments are proposed which reveal its non-classical nature.

Edge magnetism in graphene nanoribbons is a striking, yet elusive phenomenon. On the one hand, it promises exciting applications, e.g., as perfect spin filters in the context of spintronics. Also from the perspective of fundamental research, the one-dimensional nature of this ferromagnetic ordering of spins along the ribbon edges is intriguing. On the other hand, its very nature is poorly understood. On the theory level, mean-field results are partially in contradiction with more sophisticated calculations, such as quantum Monte-Carlo simulations. While the mean-field results predict a static spin polarization at the ribbon edges in the ground state, the true ground state has spin-singlet character and thus forbids any spin polarization. Also experimentally there is not yet a report of a clear signature of a magnetic phenomenon at graphene edges.

The reasons for the difficulties in the study of edge magnetism may be partitioned into two categories: (a) Insufficient control over the experimental conditions and (b) unclear signatures of edge magnetism. Indeed, it has been shown that structural edge reorganizations [4] or hybridization with substrates [5], both of which falling into category (a), may suppress edge magnetism already on a mean-field level. Moreover, since the naive expectation of a static edge magnetization is in contradiction with known ground state properties (as explained above), the experimental identification of this phenomenon is far from obvious. Also, the theoretical prediction of the response of graphene edges to experimental probes is, due to their strongly correlated nature, a generally difficult task. The special geometry of short and narrow armchair ribbons overcomes these issues. The experimental control over edge structures is remarkable; nanoribbons without a single defect and even with perfect hydrogen termination have been synthesized. And from the theory perspective this special geometry allows for the derivation of a very simple effective model which allows the exact evaluation of response and spectral functions.

FIG. 1: (Color online) Lattice geometry of an armchair nanoribbon with $W = 3$ hexagons in zigzag direction and $L = 10$ hexagons in armchair direction. On top of the lattice the weight of the localized low-energy states $|\Psi_\uparrow(0)|^2 + |\Psi_\uparrow(0)|^2$ is shown. Both, the dot size and color scales with the weight. The blue circle indicates a typical site where the spectral function is to be measured (see text).

Our analysis [6] generally starts from a Hubbard model for the $\pi$-electrons of graphene

$$H_0 + H_U = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow},$$

where $\tau$ is a spin label, $t \approx 3$ eV is the nearest-neighbor hopping matrix element and $U \approx 6$ eV is the on-site Hubbard repulsion. In addition to this very simple model we studied the influence of perturbations to this theory, such as next-to-nearest neighbor hopping, potential fluctuations, and long-range Coulomb repulsions. We found that these terms only lead to small quantitative corrections to the results presented here.

We proceed by deriving an effective description of the low-energy physics of electrons confined to the geometry shown in Fig. 1. The spectrum of the hopping Hamiltonian $H_0$ has the remarkable property that most eigenstates (the bulkstates) have energies $|\varepsilon_\pm| \geq 0.23 \, t$ and are therefore impassive. In addition, however, there are two states with energies $\varepsilon_\pm = \pm 1.29 eV e^{-L/1.86}$ exponentially small in the length $L$ of the ribbon. These are the degrees of freedom on which our effective theory is built. Their wave functions are shown in Fig. 1, from where it becomes clear that these low-energy states are localized at the zigzag...
ends of the ribbon. We introduce the two states $e_{L}^{\uparrow}$ and $e_{R}^{\uparrow}$, the linear combinations $2^{-\eta/2} (e_{L}^{\uparrow} \pm e_{R}^{\uparrow})$, of which are the mentioned low-energy eigenstates of $H_{H}$. The fermionic low-energy theory may then be written as

\[ H = t' \sum_{\sigma} e_{\sigma}^{\dagger} e_{\sigma + 1} + H_{\text{coupling}} - \sum_{\sigma} e_{\sigma}^{\dagger} (\mathbf{B} \cdot \mathbf{\sigma}/2) e_{\sigma}^{\uparrow} + U \sum_{\sigma} (e_{\sigma}^{\dagger} e_{\sigma}^{\uparrow} - 1/2)(e_{\sigma+1}^{\dagger} e_{\sigma+1}^{\uparrow} - 1/2), \]

(2)

where $t' = |e_{\pm}|$ describes an effective hopping of electrons from one end to the other, \(U = \sum_{\sigma} |\psi_{\sigma}^{\dagger}(i)|^{2} \approx 0.1U \) is an effective Hubbard repulsion for the end-localized electrons, \( \mathbf{\sigma} \) is the vector of Pauli matrices, and \( \mathbf{B} \) is an external Zeeman field. In the charge-neutral configuration the four possible states $e_{L}^{\uparrow, \downarrow} e_{R}^{\uparrow, \downarrow}$ are occupied by two electrons.

$H_{H}$ describes the hopping, on-site repulsion and Zeeman interaction of electrons confined to two localized states. However, the hopping $t'$ becomes exponentially small with the ribbon length. Thus, for large $L$ one electron will be confined to one particular end and only the electron spins are allowed to fluctuate. This is the content of a further simplified Heisenberg theory

\[ H_{H} = J_{H} \mathbf{S}_{L} \cdot \mathbf{S}_{R} - \mathbf{B} \cdot (\mathbf{S}_{L} + \mathbf{S}_{R}), \quad J_{H} = 4(t')^{2}/U^{*}, \]

(3)

Where $\mathbf{S}_{L/R}$ are spin-$1/2$ operators describing the spins of the localized electrons at the left/right end. These end spins interact antiferromagnetically due to the virtual inter-end hopping $t'$. Due to the exponential decrease of $t'$ with $L$, this coupling varies exponentially as well. By comparing the spectra of $H_{H}$ and $H_{H}$ we find that $H_{H}$ is a very good approximation for $L \geq 8$ [6].

The exponential dependence of the antiferromagnetic coupling $J_{H}$ on $L$, combined with the discreteness of $L$ gives rise to a step-like magnetic response of an ensemble of nanoribbons with different lengths. Figure 2 shows this response for various temperatures. The striking nonlinearity in the magnetic response with plateaus of equal length on a log scale is a genuine signature of the correlation physics on which also edge magnetism is based. It can be experimentally detected by low-temperature magnetometry.

A complementary experiment, based on spin-polarized scanning tunneling microscopy, probes individual ribbons. The cantilever is to be placed on top of one of the end states and measures the spin-resolved spectral function $A_{L}^{\downarrow}(\omega)$, typically near the lattice site indicated in Fig. 1. $A_{L}^{\downarrow}(\omega)$ can be calculated easily from $H_{H}$ (see Fig. 3). Without a magnetic field, the ground state of the ribbon is a spin singlet so that an electron with an arbitrary spin direction can be added and removed via the tip. This is reflected by the energy-symmetric peaks in $A_{L}^{\downarrow}(\omega)$, in the singlet phase. As $B$ is increased to be on the order of $J_{H}$, however, the ground state becomes a triplet. In this phase, only electrons of a given spin direction (quantization axis is chosen along $B$) can tunnel into the ribbon but not out of the ribbon. This spin direction is inverted as $B \to -B$. This manifests itself in the disappearance of one of the two peaks in $A_{L}^{\downarrow}(\omega)$ as $|B|$ enters the triplet regime.

**FIG. 2:** (Color online) Total magnetic moment $M$ (in $10^{3} \mu_{B}$) of an ensemble of nanoribbons as a function of the magnetic field $B$ for different temperatures. The ensemble contains 3000 ribbons for each length $L = 8, 10, \ldots, 20$. Each individual ribbon contributes two Bohr magnetons $\mu_{B}$ to the total moment if it is in the triplet state.

**FIG. 3:** (Color online) Spectral function $A_{L}^{\downarrow}(\omega)$ for $t' = 0.006$ eV and $U^{*} = 0.6$ eV, corresponding to a ribbon with $W = 3$ and $L = 10$ and. The critical field $B_{c} = \pm 2J_{H} \approx 2.1$ T is indicated by dashed lines. In the main plot the Gaussian smearing $\eta = 200$ Kelvin (text). The insets show the fine structure of the spectral peaks with narrower Gaussian smearing of $\eta = 10$ Kelvin (b) and $\eta = 0.1$ Kelvin (a).

In conclusion, we have proposed two complementary experiments which are intended to clarify the basic experimental signatures of edge magnetism in graphene. Evidently, there is no spin polarization for vanishing Zeeman fields but a subtle magnetic response.

Spin polarization limit in the warped Dirac cone of the Bi$_2$Te$_3$

L. Plucinski$^{1,2}$, A. Herdt$^1$, G. Bihlmayer$^3$, G. Mussler$^4$, S. Döring$^{1,2}$, J. Krumrain$^4$, D. Grützmacher$^4$, S. Blügel$^3$, and C. M. Schneider$^{1,2}$

$^1$Peter Grünberg Institut-6, Forschungszentrum Jülich, Germany
$^2$Fakultät für Physik and Center for Nanointegration Duisburg-Essen (CeNIDE), Duisburg, Germany
$^3$Peter Grünberg Institut-1 and Institute for Advanced Simulation-1, Forschungszentrum Jülich, Germany
$^4$Peter Grünberg Institut-9, Forschungszentrum Jülich, Germany

The magnitude of electron spin polarization in topologically protected surface states is an important parameter with respect to spintronics applications. In order to analyze the warped spin texture in Bi$_2$Te$_3$ thin films, we combine angle- and spin-resolved photoemission experiments with theoretical ab initio calculations. We find an in-plane spin polarization of up to $\sim 45\%$ in the topologically protected Dirac cone states near the Fermi level. The Fermi surface of the Dirac cone state is warped and shows an out-of-plane spin polarization of $\sim 15\%$. These findings are in quantitative agreement with dedicated simulations which find electron density of the Dirac cone delocalized over the first quintuple layer with spin reversal occurring in the surface atomic layer.

Gapless surface states in the family of three-dimensional (3D) topological insulators (TIs) Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$, and their alloys have recently attracted considerable attention due to their potential in producing fully spin-polarized currents for spin-electronic applications. Analytical theoretical models predict that these topological surface states (TSS) are topologically protected and fully spin-polarized. A more detailed analysis of such states can be performed by using density functional theory (DFT). Within this approach, the average spin polarization of the TSS was predicted to be strongly reduced due to spin-orbit entanglement, and the vector of spin polarization was found to change its orientation between the subsequent atomic layers.

Bi$_2$Se$_3$ thin films were grown on Si(111) substrates using molecular beam epitaxy (MBE) [1] and their surfaces were prepared under UHV using an optimized cleaning procedure [2].

The combination of angle- and spin-resolved photoemission spectroscopy (SP-ARPES) with ab initio theoretical calculations is an efficient approach to investigate the exotic spin texture of the TSS. Spin-polarized photoemission measurements performed at 200 K are presented in Figs. 2 (a) and (b), while Fig. 2 (c) illustrates the $k$-space volume over which the spin-polarized spectra are integrated. The polarization $P = A/S$ with the asymmetry $A = (I_L - I_R)/(I_L + I_R)$, in which $I_L$ and $I_R$ are the signals for the beams scattered from the W(001) crystal in opposite mirror directions, was computed using the Sherman function $S = 0.25$. The unpolarized constant background above $E_F$ has been removed. The combination of our cleaning procedure and the choice of the photon energy minimized the spectral weight related to the conduction band states, allowing our spin-polarized spectra to be free from the un-polarized background in the Dirac cone region.

The $P$ value extracted from the experimental data can be affected by the instrumental asymmetry of the spin polarimeter. Our calibration is confirmed by comparing the spectra measured in positions (A) and (B) as shown in Fig. 2, where clear reversal is observed in all cases, with virtually the same results on the two $k$-space points.

FIG. 1: (Color online) (a) Photoemission map of the 40 nm Bi$_2$Te$_3$ film taken at 15 K using the He I (hν $\approx$ 21.22 eV) excitation along the $\Gamma\bar{K}$ direction, with the overlaid DFT in-plane calculation, shifted by 0.45 eV to achieve the best match to the experiment. Blue and red solid circles indicate the spin direction, whereas the size of the symbols is related to the weight of the states at the surface. (b) Constant energy surfaces for the Fermi level (top), $E_F = 2.2$ eV and $E_F = 3.0$ eV. Each map was separately normalized for optimized contrast. Arrows in the $E_F = 2.2$ eV map indicate the two example symmetric positions on the ring, related to the $\delta$ band (see panel (a)), for which the direction of the polarization vector is reversed due to its helical nature.

We have confirmed that the topological protection mechanism in Bi$_2$Te$_3$ thin film samples prepared...
by an optimized in-situ procedure leads to helical single branched warped Dirac cone states [3]. Our experiments show the strong Fermi surface warping predicted by theory, with both in-plane and out-of-plane spin polarization components observed in the spin-polarized data, satisfying the antisymmetric spin property \( \langle \mathbf{k} \rangle = -\sigma \langle -\mathbf{k} \rangle \). The Dirac cone state is delocalized over the surface QL, and its spin orientation changes within subsequent layers, including the in-plane spin reversal over the first atomic layer. Despite the complications that might arise in the interpretation of photoemission spectra we notice that the experimental \( P_x \) value is in a good quantitative agreement with the theoretical prediction of 45%, when including the photoelectron information depth. Similar results have also been obtained for Sb\(_2\)Te\(_3\) thin films [4].

Further detailed studies from other groups [5,6] have shown that the magnitude and orientation of the spin polarization vector in the ensemble of electrons originating from the TI Dirac cone depends on the photon energy and polarization, and experimental geometry.

Evidence for topological band inversion of the phase change material Ge$_2$Sb$_2$Te$_5$

C. Pauly$^1$, M. Liebmann$^1$, A. Giussani$^2$, J. Kellner$^1$, S. Just$^1$, J. Sanchez-Barriga$^3$, E. Rienks$^3$, O. Rader$^3$, R. Calarco$^2$, G. Bihlmayer$^4$, and M. Morgenstern$^1$

$^1$II. Institute of Physics B, RWTH Aachen University, Germany
$^2$Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany
$^3$Helmholtz-Zentrum für Materialien und Energie, Elektronenspeicherring BESSY II, Berlin, Germany
$^4$Peter Grünberg Institut-1 and Institute for Advanced Simulation-1, Forschungszentrum Jülich, Germany

We present an angle-resolved photoemission study of the ternary phase change material Ge$_2$Sb$_2$Te$_5$, epitaxially grown on Si(111) in the metastable cubic phase. The observed upper bulk valence band shows a minimum at $\Gamma$ and a circular Fermi contour around $\Gamma$ with a dispersing diameter. This is in agreement with density functional theory calculations of the Petrov stacking sequence in the cubic phase which exhibits a topological surface state, in contrast to the topologically trivial Kooi-de Hosson sequence.

Following the proposal and discovery of topological insulators (TIs), materials are currently optimized in terms of separating the Dirac cone from bulk bands and tuning the Dirac point close to the Fermi energy $E_F$. In this course, compounds involving more than two elements are preferentially used for more flexibility. Connecting such compounds to classes of materials already in use for electronic or storage applications is desirable towards the utilization of topological properties. Important material systems for commercially used optical and non-volatile electrical data storage are phase change materials (PCMs) which are found predominantly along the pseudobinary line connecting GeTe and Sb$_2$Te$_3$ [1].

Such PCMs exhibit a large contrast in electronic and optical properties upon changing from amorphous to crystalline. Using laser-induced or electrical heat pulses, the switching occurs within nanoseconds at an energy cost of only fJ. The PCM Sb$_2$Te$_3$ is experimentally known to be a TI [2-4], and some of the other compounds on the pseudobinary line are predicted to be TIs based on density functional theory (DFT) calculations [5-9]. Ge$_2$Sb$_2$Te$_5$ (GST-225) is at the borderline of these predictions [7,9], i.e., its TI properties depend on the stacking sequence [9].

GST-225 emerges in two slightly different crystalline phases, a metastable cubic one used for applications and a stable hexagonal one. Within the stable phase, the stacking of hexagonal layers along [0001] has been proposed to be either Te-Sb-Te-Ge-Te-v-Te-Ge-Te-Sb- (Petrov phase) [10] or Te-Ge-Te-Sb-Te-v-Te-Sb-Te-Ge- (Kooi-De Hosson or KH phase) [11]. The v denotes a vacancy layer. The first prediction of topologically insulating GST-225 was made by Kim et al. for the Petrov phase while the energetically favorable KH phase was shown to be topologically trivial [6]. All DFT calculations so far have been done for the stable phase of GST-225, where exhibiting the valence band maximum (VBM) away from $\Gamma$ is connected with topologically non-trivial properties [6,7,9,12,13]. We provide the first calculations including spin-orbit coupling for the metastable rocksalt phase with Petrov and KH stacking, confirming the same trend.

FIG. 1: ARPES spectra of metastable GST-225 (111) after DI water dip: (a) recorded in $\Gamma$-K direction, (b) intensity in the $k_\parallel$ plane at $E_F$, $\Gamma$-M direction is horizontal; photon energy: 22 eV, temperature: 300 K.

GST-225 layers were grown on Si(111) by MBE in the metastable cubic phase along the [111] direction, as confirmed by X-ray diffraction (XRD). The presence of superstructure peaks in addition to the Bragg reflections of cubic GST-225 indicates vacancy ordering in the Ge/Sb/v sublattice along the growth direction. After growth, the samples have been transferred under ambient conditions. Before insertion into the ultrahigh vacuum ARPES or scanning tunneling microscopy chambers, the surface was deoxidized by dipping in deionized water following the procedure of Zhang et al. [14]. XRD data confirm that neither this procedure nor the subsequent annealing and measurements change the phase of the GST-225. Scanning tunneling spectroscopy (STS) shows a
band gap of 0.4 eV with $E_F$ at the top of the valence band.

The ARPES spectrum is displayed in Fig. 1(a). Just below $E_F$, the upper valence band shows maxima at $k_0 = 0.14 \text{Å}^{-1}$ and drops to $E-E_F = -0.3$ eV at $k_1 = 0.23 \text{Å}^{-1}$ and -0.35 eV at $k_1 = 0.1 \text{Å}^{-1}$. The constant energy cut at $E_F$ in Fig. 1(b), shows a nearly isotropic circle and faint additional intensity at high $|k_1|$ values in the six different γ-M-M directions.

DFT calculations have been performed within the generalized gradient approximation. We employed the full-potential linearized augmented plane wave method in bulk and thin-film geometry as implemented in the FLEUR code. Spin-orbit coupling was included self-consistently. As structural model for the cubic phases we adopted the atomic positions given by Sun et al. for the bulk and film structures. Two different stacking sequences were assumed for the cubic phase: a Petrov- and a KH-like sequence, which are derived from the respective hexagonal phases by tripling the unit cell and adding appropriate shifts.

**FIG. 2: DFT calculations of the band structures for cubic GST-225 with (a) Petrov- and (b) KH-type stacking sequences. Bulk bands are given as gray lines, states of the film calculations with circles. The extension of the states into the vacuum (region above the topmost Te layer) is indicated by the size of the circles. The calculations are superimposed with the ARPES spectra (2nd derivative of intensity with respect to electron energy).**

Figure 2 shows the 2nd derivative of the measured band structure along with the calculations. A reasonable agreement is only achieved with the Petrov-like stacking, including the minimum at $E_F$ of the upper valence band. The bands further down in energy (around 0.6 eV at $\Gamma$) can be associated with a Rashba-type surface state, similar to the one observed in Sb$_2$Te$_3$. In close vicinity of the upper valence band, the calculation shows the topological surface state crossing the Fermi energy at $k_0 = 0.12 \text{Å}^{-1}$. This state obviously overlaps with the upper bulk valence band within our ARPES data. In order to probe different $k_0$ and, thus, distinguish surface from bulk states, spectra with photon energies $h\nu = 17-26$ eV have been recorded. The energy of the maximum intensity at $\Gamma$ shifts with $h\nu$ as well as the wave vector $k_0$ of the band maximum. Thus, the ARPES peak at the VBM is, at least partially, a bulk band with dispersion in $k_z$ direction.

We finally compared the metastable cubic phase with previous DFT calculations of the very similar hexagonal phase. Most notably, a VBM away from $\Gamma$ consistently indicates topologically non-trivial properties for GST-225. In summary, we have shown by ARPES and STS that metastable cubic Ge$_2$Sb$_2$Te$_5$ epitaxially grown on Si(111) exhibits valence band maxima away from. All DFT calculations of Ge$_2$Sb$_2$Te$_5$ find a VBM away from $\Gamma$ only for a $\Gamma_2$ topological invariant $\nu_0 = 1$. This implies topological properties of Ge$_2$Sb$_2$Te$_5$, indicates that all phase change materials on the pseudobinary line between Sb$_2$Te$_3$ and Ge$_2$Sb$_2$Te$_5$ are topologically non-trivial, and opens up the possibility of switching between an insulating amorphous phase and a topological phase on ns time scales.

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Many-body effects in the electronic structure of topological insulators

I. Aguilera, C. Friedrich, and S. Blügel
Peter Grünberg Institut-1 and Institute for Advanced Simulation-1, Forschungszentrum Jülich, Germany

The ab-initio study of the electronic structure of topological insulators has so far been dominated by calculations based on density functional theory (DFT). While yielding accurate ground-state energies, this theory only offers a mean-field description of the electronic band structure, excluding many-body effects. We present a many-body description of the topological insulators Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ employing the GW approximation for the electronic self-energy. We restrict ourselves to one-shot, i.e., non-self-consistent, calculations, but go beyond the widely used perturbative solution of the quasiparticle equation by taking into account off-diagonal elements of the self-energy and use a consistent treatment of the spin-orbit interaction. We find that the dispersions of the bands, as well as the band gaps, are more accurately described by GW than by DFT.

The topological insulators (TIs) [1] are a recently discovered class of materials with fascinating properties: while the inside of a film or solid is an electrical insulator, fundamental symmetry considerations require the edges of finite sized films or surfaces of bulk TIs to be metallic. These surface states appear inside the band gap of the bulk band structure and have a linear energy dispersion similar to that of massless Dirac particles (Fig. 1a). In three dimensions these surface states have approximately the shape of a cone and therefore they form what is called the Dirac cone. These states are spin polarized, and there is a unique correspondence between the electrons’ momentum and their spin. The electrons travelling on such a surface state are insensitive to impurity backscattering, because their spins have opposite orientation at momenta $k$ and $-k$. TIs have thus become the focus of enormous interest in the last years, partly because of their fascinating conceptual novelty, partly because of possible applications in spintronics, quantum computing, thermoelectricity and Green IT.

Most of the theoretical results present in the literature for TIs are based on model Hamiltonians, parameter-dependent tight-binding descriptions, or density functional theory (DFT) employing either the local-density (LDA) or generalized gradient (GGA) approximations. Due to their efficiency, the LDA and GGA functionals have allowed for the study of surface and edge states of these materials and they have mostly shown good agreement with the experimental results. However, LDA and GGA are approximations to the ground-state energy and cannot in principle be expected to yield accurate excited-state properties. In particular, they suffer from a strong self-interaction error and lack many-body renormalization effects. Related to that, the DFT band gaps of semiconductors and insulators are systematically underestimated. TIs are not an exception: In TIs, a strong spin-orbit coupling (SOC) causes the bulk highest valence band (VB) and the lowest conduction band (CB) to invert in the band gap region (Fig. 1a). The bands hybridize so that an inverted energy gap forms. Due to this inverted band gaps, the DFT underestimation of the band gaps has not only quantitative but also qualitative consequences (Fig. 1c) and it can even lead to the wrong prediction of some trivial insulators as topological insulators. Recently, to overcome this problem, calculations based on the GW approximation for the self-energy have started to emerge in the theoretical study of TIs [2-8].

![FIG. 1: (a) Schematic bulk VB and CB of a TI showing the band inversion due to SOC and the spin-polarized metallic surface states. If (a) is imagined as the LDA result, the general underestimation of the LDA band gaps results in a too deep penetration of the VB and CB into each other and an overestimated inverted gap. (b) Effect of GW on this inverted gap: GW "pulls" VB and CB away from each other (like in trivial semiconductors) resulting in a corrected, smaller inverted gap (c), also causing the disappearance or flattening of the camelback shape.](image-url)

The GW approach is the most widely used approximation for the self-energy in many-body perturbation theory: The GW self-energy is represented as the product of the screened Coulomb interaction among quasiparticles $W$ and the one-particle Green function $G$, which describes the motion of an extra hole in the solid (like in a direct photoemission experiment) or an extra electron (in inverse photoemission). In this respect, the physics included in the GW approach highly resembles that of a photoemission experiment and it is therefore a very good approximation to compare to angle-resolved photoemission spectroscopy measurements (ARPES). In addition, the broadening of the bands...
We have performed one-shot GW calculations for Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ within the all-electron full-potential linearized augmented-plane wave (FLAPW) formalism implemented in the DFT code FLEUR (www.flapw.de) and the GW code SPEX [9]. In the GW calculations, the SOC has been included in a consistent way (already in the non-interacting reference system) as proposed in [2]. Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ are extensively studied TIs, due to their large bulk band gaps (100–300 meV), which allow for surface effects to remain relevant even above room temperature. In the first GW calculations for these materials [3,4], the SOC was incorporated in an a-posteriori correction after the calculation was performed in the absence of SOC. We have found [5] that this a-posteriori approach yields an overall reasonably accurate electronic band structure, but the dispersion of the bands involved in the band inversion are not obtained correctly when compared to the more consistent treatment of SOC implemented in SPEX. In particular, Bi$_2$Se$_3$ is near a transition to a trivial insulator when the simplified approach is used.

The GW approximation is usually applied in a perturbative approach because this requires only the diagonal elements of the self-energy to be calculated. However, we have found that the off-diagonal elements of the self-energy play a very important role in certain regions of the band structure of Bi$_2$Te$_3$ [6]. In addition, the inclusion of the off-diagonal elements of the self-energy allowed us [6] to discuss properties derived from the quasiparticle wavefunctions, like the band inversion and the $Z_2$ topological invariants, which define the trivial or topological character of materials. The DFT values of the $Z_2$ invariants remained unchanged upon applying quasiparticle corrections within GW.

The conclusions of those two more methodological studies [5,6] allowed us to accurately characterize the band structures of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ in the whole BZ within the GW approach and perform a thorough comparison with ARPES [7,8]. In general, we have seen that for this family of TIs, the differences between the DFT and GW results are maximal close to the Fermi energy around the $\Gamma$ point (i.e., in the band-inversion region, see the example of Bi$_2$Se$_3$ in Figs. 2a and 2b). We have found that for Bi$_2$Te$_3$, the camelback shape of the VB flattens significantly, and it disappears for Bi$_2$Se$_3$ (red solid line in Fig. 2b) and Sb$_2$Te$_3$. The disappearance or flattening of the camelback shape is also illustrated in Fig. 1c. In the case of Bi$_2$Se$_3$, we have arrived at GW theoretical data in good agreement with experimental observations [7], both indicating that Bi$_2$Se$_3$ is a direct-gap semiconductor with the valence band maximum (VBM) and conduction band minimum (CBM) located at the $\Gamma$ point (Fig. 2b). This result is very important for the scattering and transport properties of the topological surface states and may call for a new interpretation of results of, e.g., quasiparticle interference, which relied so far on the wrong bulk band structure derived from DFT (Fig. 2a).

In summary, the one-shot GW calculations with a consistent treatment of SOC and taking into account the off-diagonal elements of the self-energy constitute a significant improvement over DFT results. They produce quasiparticle band structures of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ in better qualitative (dispersions of the bands and positions of VBM and CBM) and quantitative (values of the gaps) agreement with ARPES. This evidences the importance of many-body effects on the band structure of TIs and invites to reinvestigate their surface states within a GW framework.

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Lattice dynamics in Bi\textsubscript{2}Te\textsubscript{3} bulk and of nanowires

D. Bessas\textsuperscript{1,2,3} and R. P. Hermann\textsuperscript{1,2}

\textsuperscript{1} Jülich Centre for Neutron Science-2 and Peter Grünberg Institut-4, Forschungszentrum Jülich, Germany
\textsuperscript{2} Faculty of Science, University of Liège, Belgium
\textsuperscript{3} European Synchrotron Radiation Facility, Grenoble, France

Tetradymite structured (Sb,Bi)\textsubscript{2}Te\textsubscript{3} is currently, and since more than 60 years, the most efficient material for thermoelectric energy conversion close to room temperature. Despite this, relatively few investigations have been carried out in order to understand the link between the lattice dynamics and the low thermal conductivity in these materials. This low thermal conductivity is, next to an excellent compromise between electrical conductivity and thermopower, a key property that contributes to the large thermoelectric figure of merit. In addition, renewed interest in this material class comes from topological insulator behavior and applications as phase change material for information storage. Detailed investigations of the lattice dynamics reveal element specific mode attributions, key properties such as the average acoustic phonon group velocity, and the element specific force constants. Further, a comparison between phonons in bulk and nanowires indicates that size reduction leads to a reduction in speed of sound, and, hence, we predict a corresponding reduction in thermal conductivity. Our studies are, to our best knowledge, the first to report full phonon spectra in oriented nanowires.

Because the majority of thermoelectric applications, at least for the largest market, require operation near room temperature, significant effort is devoted since many years in optimizing, characterizing and understanding the properties of bismuth telluride and related phase, which is unsurpassed in terms of thermoelectric conversion efficiency near room temperature. It is therefore also natural that after the first suggestions to investigate in detail thermoelectric materials in nanoscaled systems, where an improvement in the figure of merit with reduced dimensions is predicted, various bismuth telluride based nanostructures, e.g. thin films, nanodots or nanowires have been investigated.

An important aspect of the properties of bismuth telluride is the layered structure and rather large structural anisotropy with a c/a=7 ratio in the lattice constants in the conventional pseudo-hexagonal setting. The structure itself is comprised of repeated -[Te-Pr-Te-Pr-Te]- quintet units linked by Te-Te van der Waals interactions. The structural anisotropy is also reflected in the transport properties, although not to the full extent.

From the point of view of thermal conductivity, which is the main interest of our studies, the determining parameters are the phonon group velocities or the speed of sound, the specific heat, and the average phonon interaction relaxation time, a quantity which is related to the anharmonicity of the material. The hallmark of the anharmonicity is captured by the Grüneisen parameter, that relates thermal expansion, elasticity and specific heat.
element specific density of phonon states in these materials. The experimental method, nuclear inelastic scattering, relies on the Mössbauer effect and yields the vibrational spectrum via the phonon assisted nuclear resonant absorption. Due to its isotope specificity, this method provides element specific access to the density of phonon states, at least for elements that possess a suitable Mössbauer active nuclear resonance, such as antimony-121 and tellurium-125. The obtained phonon spectra for antimony and tellurium in the tetradymite materials yields, first, an easy mode attribution of specific modes to the vibration of an element, second, it provides access to important thermodynamic quantities such as the average speed of sound and the element specific force constants, and, third, indicates the acoustic cut-off energy, above which phonon modes are optical and have a rather less dispersive character and contribute less to thermal transport. Comparison of our phonon data with existing literature reveals that the origin of the low thermal transport in antimony and bismuth telluride is related more to the low speed of sound and acoustic cut-off rather than to anharmonicity, as the determined the Grüneisen parameters are quite normal with $\gamma \approx 1.5-1.7$.

A second question concerns the impact of reducing dimensions on the lattice dynamics and, hence, on the thermal properties. For this purpose, we have investigated the phonon spectra by tellurium-125 nuclear inelastic scattering applied on 50 nm diameter Bi$_2$Te$_3$ nanowires. The oriented nanowires were grown, using bismuth and isopically enriched tellurium-125, inside an alumina membrane by using a novel electrodeposition method. The structure and orientation was investigated using high-energy synchrotron radiation diffraction, see Fig. 2, revealing that the wires are highly oriented, but with the crystallographic c-axis perpendicular to the nanowire axis, and thus in the membrane plane.

The embedded wires were then used for phonon spectroscopy and the density of states of the phonons with atomic vibrations projected onto the nanowire direction and perpendicular to it were determined, see Fig. 3. These data first reveal the excellent crystallinity of the samples, as the nanowire data can essentially be understood by an appropriate linear combination of data measured on a Bi$_2$Te$_3$ single crystal. However, an essential difference subsists, namely that the Debye level, obtained from the low-energy limit of the density of states, is significantly enhanced with respect to the bulk material. This can be interpreted as a significant decrease in the average phonon group velocity, or in a somewhat simplified way, the speed of sound, of in the nanowires. As the speed of sound is an essential parameter in thermal transport, our study thus suggests that thermal transport is impeded by about 10% in the nanowires. There is however much room for further improving properties by further impeding thermal transport in thinner nanowires, which were still rather large, with 50 nm diameter.

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References:

We report on a domain suppression in topological insulator Bi₂Te₃ thin films grown on Si(111) substrates by means of molecular-beam epitaxy (MBE). We found out that usually the Bi₂Te₃ epilayers form domains – in-plane rotated 60° - on the Si (111) substrates, which are suppressed by reducing the Bi₂Te₃ growth rates. This observation can be explained by the van der Waals interaction between the 1st Te layer and the 1st Si layer underneath the Si surface atoms.

Bi₂Te₃ belongs to the family of topological insulators (TIs) which have an exotic electronic structure. TIs are insulating in bulk and have topologically protected Dirac-like spin-polarized surface states. Because of these surface states, TIs have great potential to develop novel devices in the field of electronics or spintronics [1]. However, the structural perfection of TIs is a key issue for the employment in future applications. For example, state of the art Bi₂Te₃ material usually suffers from structural imperfections, such as point defects and twin domains [2]. These defects are a possible source of the high bulk carrier concentration, which makes the detection of surface carriers - with these fascinating properties - difficult. Hence, reducing the amount of defects is of utter importance to study features of TIs.
scans, six peaks are seen in the Bi$_2$Te$_3$ sample grown at high growth rates ($v = 26$ nm/h, figure 2a), whereas only three peaks are observed in the sample grown at low growth rates ($v = 2.7$ nm/h, figure 2b). The effect is even more apparent in the one-dimensional pole figure scan (figure 2c), which shows a gradual transition from six peaks to three peaks for lower growth rates. Hence, the reduction of the growth rate causes a suppression of the domain formation in the Bi$_2$Te$_3$ epilayers. Interestingly, the peaks of high intensity are always collinear with the (311) reflection of the Si(111) substrate, suggesting a preferential orientation of the Bi$_2$Te$_3$ epilayer on the Si(111) surface.

The existence of the two domains was also observed in the scanning tunneling microscopy (STEM) image (figure 3a). The figure shows that the presence of two domains is found only within the first five to six monolayers, at a later stage to three peaks for lower growth rates. Hence, the analysis also allows the investigation of the Si/Bi$_2$Te$_3$ interface. A high-resolution high-angle annular dark field image of a Bi$_2$Te$_3$ film is shown in the (110) projection of the Si substrate (figure 3b). According to their difference in atomic number, Bi atoms appear brighter than Te and Si atoms. From the analysis of the blue and read area in figure 3b, line scans across the interface are obtained with different intensity levels of Bi, Te, and Si (figure 3c). With these line scans, positions of individual Si, Bi, and Te atoms can be identified. The atomic configuration of the Si/Bi$_2$Te$_3$ interface is shown in figure 3d. The image depicts a common behavior between the Si surface atoms and the first Bi$_2$Te$_3$ QL in order to saturate the dangling bonds of the Si surface atoms prior to the growth of Bi$_2$Te$_3$.

In order to calculate the vdW potential $\phi = -C/r^6$, Te networks were placed on random positions of the Si lattice and subsequently displaced within the Si unit cell (figure 4). These networks have a length of 8 Te atoms in order to realize lattice matched conditions to the Si substrate (7 Te unit cells are lattice matched to 8 Si unit cells). Hence, these networks can be regarded as a building block of these two domains, as the domains are composed of a multiple of these building blocks. For each position the vdW potential was calculated, taking the nearest neighbor or the next nearest neighbors of the Si lattice into account, and the position with the lowest vdW potential was determined. The calculations show that for both Te networks the position with the lowest vdW potential is obtained for the configuration with the highest symmetry, i.e. the outermost Te atoms are positioned right above the Te-terminated Si atoms, as depicted in figure 4.

To quantitatively analyze the vdW potential, two cases were distinguished. First, the Te passivation layer and the topmost Si layer were taken into account. Second, the Te passivation layer, the topmost Si layer, and the first Si layer underneath the Si surface were considered (cf. figure 3d). In the first case, no differences between the Te networks 1 and 2 are obtained, which can be understood in terms of the 60° symmetry of the (Te-terminated) Si surface atoms (compare the identical arrangement of Si surface atoms - colored in red - for the row 3 in both networks). However, in the latter case, the calculations show a difference in the vdW potential between the two networks, owing to the 120° symmetry of the (Te-terminated) Si surface atoms and the first Si layer underneath (compare the different arrangements of the Si atoms underneath the surface - colored in yellow - for the networks 1 and 2). The analysis shows that network 2 has a lower vdW potential, i.e. network 2 is energetically more favorable than network 1. Thus, we attribute network 2 to present the preferential orientation for the nucleation of Bi$_2$Te$_3$ on the Si(111) substrate.

This finding is beneficial for realizing high-quality domain-free Bi$_2$Te$_3$ TI material. It is also in stark contrast to the strong directional covalent bonds in conventional epitaxy that takes into account the nearest neighbor only. Hence the vdW growth may provide more freedom to grow high-quality TI films on a large variety of substrates without lattice-matched conditions in order to explore the fascinating properties inherent in TIs.

Buried Triple-Gate Structures for Advanced Field-Effect Transistors

M.R. Müller1,2, A. Gumprich2, F. Schütte2, K. Kallis2, U. Künzelmann3, S. Engels4, C. Stampfer4, N. Wilck1, and J. Knoch1

1 Institute of Semiconductor Electronics, RWTH Aachen University, Germany
2 Intelligent Microsystems Chair, TU Dortmund University, Germany
3 Institute of Semiconductor and Microsystems Technology, TU Dresden, Germany
4 II. Institute of Physics B, RWTH Aachen University, Germany

A key element for the investigation of novel channel materials and device principles is the realization of appropriate source-drain doping profiles. Here, the manufacturing of a buried triple-gate (BTG) structure, where three separately addressable gates are realized to control the charge carrier density within source, drain and the channel via electrostatic doping, is described. The BTG structure is optimized with respect to the visibility of a monolayer graphene with optical microscopy but are also suitable for the investigation of other nanoobjects. As an example, electrical measurements of a 30nm graphene nanoribbon are presented.

Extraordinary electronic transport properties and an extremely small geometrical size have spurred an increasing interest in carbon-based materials such as carbon nanotubes (CNT) and graphene as an alternative to silicon for future nanoelectronics devices. The reason for this is that carbon-based materials potentially allow the realization of ultimately scaled, high performance field-effect transistors. In addition, the small size, low effective masses and a symmetric band structure with a tunable, direct band gap have rendered graphene and carbon nanotubes as a highly attractive choice for novel device concepts such as band-to-band tunneling field-effect transistors (TFETs).

However, doping carbon-based nanostructures appropriately is a delicate task since first, doping by replacing any carbon atoms (if possible) would destroy the desired electronic properties of nanotubes or graphene. Secondly, the low density of states (DOS) of graphene and of carbon nanotubes due to their one-dimensional electronic behavior is a major issue when considering TFETs leading to a trade-off between on-state performance and switching behavior. On the other hand, the low DOS enables an almost perfect gate control. Hence, electrostatic doping can be used to realize source and drain contact regions by inducing charge carriers via electric fields.

Here, we describe the development and manufacturing of a buried triple-gate (BTG) structure with three individually controllable gates serving as a platform for the investigation of various nanobjects. As an example, graphene nanoribbons are studied in more detail.

FIG. 1: Schematic illustrations of the manufacturing process of the BTG structures. Anisotropic wet chemical etching is used to form V-shaped grooves in the SOI to minimize the un-gated region in-between the three gates.

Fig. 1 illustrates the manufacturing process of the BTG structure [1]. The starting material is a 4-inch SOI-wafer with a top-layer of 340 nm (100)Si and a 400 nm buried oxide (BOX). The silicon is implanted with phosphorous (10 15 cm-2, 75 keV, 7.5°). After RCA-cleaning a 20 nm SiO2 layer is grown using dry thermal oxidation thereby activating the dopants. Optical lithography is used to pattern the oxide layer using buffered oxide etch (BOE). Tetramethylammonium hydroxide, 25 wt.% at 80°C is used to anisotropically etch through the SOI layer yielding a V-shaped groove; this V-groove minimizes un-gated regions in-between the source-channel and channel-drain gates. The oxide mask is removed and a wet thermal oxidation is carried out leading to a 100nm thick oxide layer as required for optimum visibility of a graphene mono-layer [2]. Subsequently, aluminum is sputter-deposited onto the surface and chemical-mechanical planarization is used to remove the Al overburden [3]. The gate dielectric on top of the aluminum gate was obtained by plasma oxidation or deposition of Al2O3 with ALD. The BTG-structures were completed by selectively etching the oxides using CHF3+Ar plasma in the contact regions and a subsequent deposition of 180 nm Ti+Au contact metal using a lift-off technique. The finished wafer was cut into sample pieces of 7.5x7.5 mm2 (details can be found in Ref. [1]).
Graphene is exfoliated from natural graphite and transferred to the BTG structures using the PVA/PMMA method. With a special alignment station, a deposition onto the desired location is accomplished with an accuracy of approximately ~5 µm. Afterwards, electron-beam lithography (EBL), thermal evaporation and lift-off is used to fabricate source/drain contacts of 7.5 Å Ti + 85 nm Au. Eventually, a final EBL is carried out to pattern a 30 nm wide and ~5 µm long nanoribbon. After development of the PMMA in a water/IPA mixture at -15 °C, reactive-ion etching with Ar:O₂ (1:1) plasma is used to etch the exposed graphene. Subsequently, the PMMA mask is removed using dimethyl sulfoxide.

Fig. 2 shows a top-view and cross-sectional electron micrograph of a BTG structure with a 30nm wide graphene nanoribbon (see inset of Fig. 2) insulated by a 100nm SiO₂ layer in the source and drain side-gate areas and ~5nm Al₂O₃ in the region of the central gate [1,4]. First, to show that gate-controlled doping is feasible, conventional n- and p-type FETs were realized by applying the same positive and negative voltages to the source/drain side-gates, i.e., $V_{\text{side-gate source}} = V_{\text{side-gate drain}}$ and measuring the transfer characteristics at each side-gate voltage. The lower panel of Fig. 3(a) shows a 2-D plot of the measurements taken at a temperature of 25 K; exemplarily, the top panel of Fig. 3(a) shows trans-fet characteristics for $V_{\text{source/drain side-gate}} = -12.2$ V (blue line), $-1.8$ V (gray line) and $22.7$ V (red line), respectively. One clearly observes that by applying appropriate side-gate voltages conventional n-FETs (red line), p-FETs (blue line), and a device without significant current flow due to intrinsic source/drain regions (gray line) can indeed be realized. Next, different voltages are applied to the source and drain side-gates in order to obtain an n-p doping profile as appropriate for a TFET. A typical transfer characteristic of such a device is shown in Fig. 3(b) with a steep turn on around a gate voltage of $V_{GS} = 2.5$V. However, for a true TFET the bandgap of a 30nm wide graphene nanoribbon is still too small to realize low off-state currents and thus it is difficult to extract a proper inverse subthreshold slope since the off-state behavior of the device is deteriorated by leakage currents. Nevertheless, the experiment shows that the triple-gate structures enable investigations of TFET devices due to gate-controlled doping.

In conclusion, to realize electrostatic source-drain doping, a buried triple-gate (BTG) structure was manufactured and a 30 nm graphene nanoribbon was fabricated on top of the BTG structure. Electrical measurements show that the three different sections can be n- and p-doped enabling investigation of e.g. band-to-band tunnel FETs.

Experimental Demonstration of Inverter and NAND Operation in p-TFET Logic at Ultra-low Supply Voltages

Peter Grünberg Institute-9, PGI 9-IT, Forschungszentrum Jülich, Germany

Tunnel-FETs (TFETs) have been studied extensively as a replacement of MOSFETs in the supply voltage regime below $V_{DD} = 0.3$ V [1]. Due to the TFET ability for offering inverse subthreshold slopes (SS) below 60 mV/dec, these devices are promising candidates for power efficient integrated circuits. Extensive research has been carried out on the characteristics of single TFET devices [2][3] and first inverter structures have been realized as demonstration of simple logic circuits [4][5][6]. In this work, we present TFET logic circuits based on gate-all-around (GAA) Si nanowire (NW) array TFETs showing small SS and high $I_{on}$ of 39 $\mu$A/µm at $V_{DD} = -1$ V. This comparably high performance in Si TFETs was realized by a source formation via silicidation and dopant segregation. Using these devices inverters based on p-TFET logic and for the first time TFET NAND gates are demonstrated experimentally. The logic gates operate at ultra-low supply voltages down to $V_{DD} = 0.15$ V.

The NW TFETs are fabricated on SOI substrate and consist of an array of 250 NWs with a diameter of 20 nm. A gate stack consisting of 3 nm ALD HfO$_2$ and 50 nm TiN is wrapped around the NWs and patterned to a gate length of 250 nm as shown in the SEM image in Fig.1. Single crystalline NiSi$_2$ layers were formed at source/drain (S/D) with high alignment accuracy to the gate without encroachment. Tilted implantation with P$^+$-ions into the silicide layer using the gate as a shadow mask was employed to form an n$^+$-doped source pocket after low temperature annealing via dopant segregation. A steep source doping profile with 2.4 nm/dec was achieved using this technique.

The $I_D-V_G$ characteristics of the GAA NW TFET with 250 nm gate length shown in Fig.2 exhibit steep switching characteristics and high $I_{on}$. The asymmetric design with n$^+$-doped pocket at the source and Schottky-contact at the drain suppresses the ambipolar TFET characteristics enabling low $I_{off}$ and high $I_{on}/I_{off} > 10^5$. The minimum SS is 69 mV/dec. $I_{on}$ reaches 39 $\mu$A/µm at $V_{DD} = V_G = V_{DS} = -1$ V in the $I_D-V_{DS}$ characteristics shown in Fig.3. Fig.4 depicts the schematics of a p-logic inverter and NAND gate consisting of a resistor and one or two p-TFETs, respectively.
FIG. 4: (a) Schematic of a p-logic Inverter and (b) a p-logic NAND gate.

FIG. 5: Voltage transfer characteristics (VTC) of a p-TFET inverter with resistors adjusted for each VDD.

Fig. 5 shows the measured voltage transfer characteristics (VTC) of the p-TFET inverter at VDD from -0.5 V down to -0.15 V. The resistor R is adjusted for different VDD, in order to achieve switching voltages close to VDD/2, which corresponds to the maximum noise margins. Fig. 6 shows the time response measurement of the inverter output Vout for different VDD. The rise time t\text{rise} decreases for the smaller pull-up resistor due to decreased load times at higher current levels. The fall time t\text{fall} of Vout is determined by the current flow through the p-TFET and thus decreases with higher VDD. Since the resistance of the p-TFET in the on-state has to be smaller compared to R in order to pull the output to ground t\text{rise} is always larger compared to t\text{fall} and thus limits the switching speed of the device. Fig. 7 exhibits the time response measurement of a p-TFET NAND gate as depicted in Fig. 4 (b). The input pattern for V_\text{in,A} and V_\text{in,B} are shown as an example for VDD = -0.5 V and Vout of the NAND gate is shown for VDD = -0.2, -0.3 and -0.5 V. Clearly the truth table of a NAND gate is observed.

FIG. 6: Time response measurement of p-logic inverter.

FIG. 7: Time response measurement of p-logic NAND gate.

In summary, we demonstrated p-logic TFET inverter operation down to ultralow VDD = -0.15 V and for the first time a NAND TFET gate operating at VDD = -0.2 V. Complementary TFET logic circuits should improve the inverter as well as NAND gate switching speed by eliminating the slow t\text{rise} caused by R.

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Crystal phase selective growth in GaAs/InAs core-shell nanowires

T. Rieger, Th. Schäpers, D. Grützmacher, and M. I. Lepsa
Peter Grünberg Institut-9, Forschungszentrum Jülich; Germany

GaAs/InAs core-shell nanowires (NWs) were grown by molecular beam epitaxy and investigated by means of high resolution transmission electron microscopy (HRTEM). The GaAs core NWs show a controlled switching between the zinc blende (ZB) and the wurtzite (WZ) crystal structure induced by partial droplet consumption. During InAs shell growth, this polytypism gives rise to a strongly reduced growth rate on the WZ phase where each short WZ segments acts as a barrier for the shell growth. By this, the shell can be axially interrupted. This novel type of core-shell NWs opens the way to axially stacked and electrically separated devices, controlled constrictions of the shell thickness as well as a further understanding of the polytypism in NWs and its influence on the growth dynamics.

III-V semiconductor nanowires are promising building blocks for the fabrication of nanodevices, especially when they contain heterostructures. Such heterostructures can be in an axial or in a radial configuration. The latter one means that a NW core is surrounded by one or multiple shells. These core-shell NW structures can either passivate the core or form tubular active regions like conductive tubes [1]. However, if the core contains different crystal structures, a typical situation in NWs, the growth of the shell can be influenced by the underlying crystal structure of the core. The ZB crystal structure is characterized by an \( \text{ABCABC} \) stacking sequence, while the WZ lattice has an \( \text{ABAB} \) stacking sequence. Some research groups showed differences in the growth of shells around ZB and WZ cores, these were, however, limited to the growth rate [2]. Here, we show that InAs preferentially nucleates and grows on ZB GaAs whereas nucleation and growth on the WZ phase of GaAs is hindered.

Self-catalyzed GaAs NWs were grown by molecular beam epitaxy on GaAs (111)B substrates. By applying a growth interruption method, the crystal structure of the GaAs NWs is alternated between ZB and WZ [3]. Typically, self-catalyzed GaAs NWs have a twinned ZB crystal structure. However, by partially consuming the catalyzing Ga droplet in the presence of arsenic, the crystal structures switches to WZ. Subsequently, a 10 nm thick InAs shell was grown at a temperature of 490°C around the NWs [4].

When supplying both elements for GaAs NW growth, Ga and As, the Ga droplet on top of the GaAs NWs has a contact angle of about 140° and nucleation occurs in the droplet resulting in the ZB crystal structure (Fig. 1A). By increasing the V/III ratio, thus increasing the As flux, the contact angle decreases and a new layer nucleates at the triple phase line between the droplet, vacuum and the crystal which creates a WZ stacking (Fig. 1B). Controlling the supply of both elements and therefore the shape and contact angle of the droplet opens the possibility to alternate the crystal structure between ZB and WZ. Figures 1C and D show TEM micrographs of WZ segments of 20 nm and 300 nm length demonstrating the ability to tailor the length of the WZ segments within a wide range. However, as can be seen, the interface from a long, pure ZB segment to a pure WZ segment is not abrupt but it is characterized by a transition region. This transition region is composed of twinned ZB, stacking faults as well as short WZ segments. In general, the transition region from ZB to WZ is more abrupt than reverse, and less WZ segment segments are found in the transition region from ZB to WZ than vice versa.

FIG. 1: A. Schematic illustration of the droplet geometry resulting in a ZB crystal structure. B. Schematic illustration of the droplet geometry resulting in a ZB crystal structure. C. HRTEM micrograph of a GaAs NW with a short WZ segment embedded in a ZB matrix. D. TEM micrograph of a 300 nm long WZ segment.

A subsequent overgrowth of the GaAs NW core with InAs is found to create constrictions along the NW axis. These constrictions are correlated with the alternating crystal structure in the core: ZB GaAs is overgrown with InAs while the growth of InAs on the WZ phase of GaAs is hindered. Exemplarily, this is shown a scanning electron microscopy (SEM) micrograph in Fig. 2A.
diameter is clearly reduced and an upper and a lower border can be seen. For an easier interpretation, false colors were used to distinguish regions with and without the InAs shell. Most dominant are, in fact, the different shapes of the upper and lower shell boundaries. The boundary from the ZB region (with the shell) to the WZ region (without InAs shell) forms a tongue like shape, which means that the lateral dimensions of the shell decrease and cover only parts of the NW side facets but not the NW edges. Contrary, the boundary from the WZ region (without InAs shell) to the ZB region (with InAs shell) does not exhibit this pronounced shape but a more abrupt change.

FIG. 2: A. SEM micrograph of a GaAs/InAs core-shell NW with a WZ segment in the GaAs core. False colors are used to indicate the outer material: InAs red, GaAs blue. B. HAADF image with superimposed EDX line scans verifying the absence of InAs at the constriction.

The situation becomes even more evident by the use of high angle annular dark field (HAADF) images in combination with energy dispersive x-ray spectroscopy (EDX). Figure 2B shows a HAADF image with four superimposed EDX line scans, three of them horizontal as well as one in the vertical direction. As seen, the upper and lower line scans clearly demonstrate a core-shell structure while the scan in the center, which is positioned at the constriction, does not show any In signal, thus no shell. Similarly, the vertical line scans shows a dip in the In signal. Nucleation of InAs is found to take place only on the ZB regions of the GaAs core, growth on the WZ phase originates from the ZB regions in each case. Thus, the nucleation and growth of InAs on GaAs is crystal phase selective [5]. The origin of the different shapes is determined by the crystal structure of the core. The stitched TEM micrographs in Fig. 3A and B display the transition regions from ZB to WZ and from WZ to ZB in the core-shell nanowires, respectively. Identically to the SEM image in Fig 2A, the NW diameter at the WZ phase is reduced compared to the ZB phase. However, the decrease in diameter is not continuous but proceeds in steps. Each of these steps is found to end at a short WZ segment within the transition region (arrows in Figs. 3A and B). Thus, the WZ segments act as barriers for the growth of the InAs shell. As stated above, the number of WZ segments in the transition region differs for the switching of the crystal structure from ZB to WZ and vice versa. In this sense, an interface with a low number of WZ segments has only few growth barriers and the growth front can reach the long WZ segment earlier than in an interface region with a high number of WZ segments. Once the WZ segment is reached by the InAs growth front, growth proceeds slowly. The growth rate in the (0001) direction of the WZ phase is found to be larger than in the (1100) direction, as evident by the tongue-like profile as well as the uncovered edges in Fig. 2A. For both crystal structures, the growth of InAs on GaAs is epitaxial, thus the InAs adopts the crystal structure of the GaAs core. The lattice mismatch of about 7% is accommodated by misfit dislocations [4]. However, despite these high dislocation densities recent investigations revealed an electronic phase coherent length of several hundred nanometer [1].

FIG. 3: A. Stitched TEM micrograph of the interfacial region from ZB to WZ in a GaAs/InAs core-shell nanowire. B. Stitched TEM micrograph of the interfacial region from WZ to ZB in a GaAs/InAs core-shell nanowire. The arrows point to short WZ segments in the transition region.

We consider this crystal phase selective growth to be caused by direction-dependent lattice mismatches in the WZ phase as well as well as unbalanced neighbors [5]. Contrary to the WZ phase, the lattice mismatch is equal in all directions in the ZB lattice. It is specific to NWs due to their polytypism between the ZB and WZ crystal structures. Using this technique, electrically active shells can be stacked axially and controlled constrictions of the shell thickness can be prepared, allowing further investigations of quantum confinement effects.

Growth and characterisation of GaN/AlInGaN/GaN double heterostructures for p-channel transistors

H. Hahn¹, B. Reuters¹, A. Pooth¹, B. Holländer², U. Breuer³, M. Heukuën⁴, H. Kalisch¹, and A. Vescan¹

¹ GaN Device Technology, RWTH Aachen University, Germany
² Peter Grünberg Institut-9, PSI-9-IT, Forschungszentrum Jülich, Germany
³ Zentral Institut für Engineering, Elektronik und Analytik-3, Forschungszentrum Jülich, Germany
⁴ AIXTRON SE, Herzogenrath, Germany

GaN-based devices have attracted huge interest in the past. Thereby, the focus of research has been on n-channel devices. By introducing p-channel devices, new possibilities in circuit design can be opened up. Yet, the mechanism for two-dimensional hole gas formation remains unclear and poor device performance still hinders the application of such devices. Hence, in this report the strategy for achieving p-channel devices is presented. The formation of hole conductivity and p-channel device performance for a wide range of hole concentrations are discussed.

For more than 20 years, field effect transistors (FETs) on basis of GaN have attracted huge interest. GaN offers unique properties such as a high breakdown field and a large built-in polarisation. In a heterostructure, two materials with different magnitudes of polarisation lead to a fixed polarisation-induced interface charge. In this case, the above mentioned properties are complemented by the possibility to form a two-dimensional electron gas with a very high carrier mobility at very dense sheet carrier concentrations. In the past, the technology has been optimised mainly for n-channel devices. On basis of heterostructure FETs (HFETs), circuits for applications such as RF power amplification and power-switching are already on the market.

With the increasing maturity of the material, also p-type conductivity in two-dimensional hole gases (2DHGs) comes into focus. Some studies on 2DHGs and HFETs employing these have been reported [1-5]. However, there is both a need of further understanding the mechanism of forming a 2DHG as well as of demonstrating p-channel HFETs with reasonable device performance. Both aspects are dealt with in this report.

The growth of the structures was carried out via metal organic chemical vapour deposition (MOCVD). On a sapphire substrate, the growth was initiated with an AlN nucleation layer. Thereafter, a semi-insulating GaN buffer was grown on which an AlInGaN barrier layer was deposited. The composition of the barrier layer was varied for different samples (A to E) with results as listed in Tab. 1 (additional reference samples are also included). The process was finished by depositing GaN layers with different p-type doping densities. The final epitaxial layer stack is shown in Fig. 1 (left). Test structures and transistors were processed by the following steps. After a dry-etch mesa isolation, ohmic contacts were formed with a Ni/Au stack. With the ohmic contacts as hard mask, the graded GaN:Mg++ layer was removed using a digital recess etch [7]. Finally, Mo/Au gate contacts were deposited. The characterisation of the epitaxial layer stack was performed by Rutherford backscattering (RBS) and secondary ion mass spectroscopy (SIMS). Test structure and transistor characterisation were performed by van der Pauw, Hall and I-V measurements.

The presence of a polarisation-induced 2DHG was confirmed by comparison of the heterostructure described above with reference sample F, consisting of GaN bulk layers p-doped identically to the heterostructure. This sample (without AlInGaN backbarrier) showed no measurable hole density. Also, a control heterostructure (sample G) without Mg-doping of the top layers revealed no accessible hole density. In contrast, the corresponding (doped) sample B shows a 2DHG density of about $1 \times 10^{13}$ cm$^{-2}$. This allows two conclusions: first, the 2DHG is formed by the polarisation difference between top GaN channel and AlInGaN barrier; second, the 2DHG is only formed when Mg-doping is applied to compensate.
for the n-background of nominally undoped GaN, which would otherwise prevent the 2DHG formation [8] and therein).

The Mg-doping concentration profiles were analysed by means of SIMS. The results are depicted in Fig. 2. A Mg concentration above the detection limit becomes visible at about 25 nm, although the Mg doping was turned on at a depth of about 30 nm before the end of the growth. Hence, the Mg acceptors are spatially separated from the holes in the 2DHG by more than the nominal 3 nm. The doping level is in the low to mid 10^{19} cm^{-3}. "TMGa ramp down" indicates the point at which the Mg incorporation is increased by reducing the Ga flow. The Mg concentration then rises up to 10^{21} cm^{-3} near the surface [8].

The exact compositions of the five samples grown was analysed by means of RBS. The values are listed in Table I. The composition varies over a wide range from a high-polarisation Al-rich layer for sample A to a Ga-rich nearly lattice-matched-to-GaN layer for sample E. In the same sample, sheet carrier densities \( p_s \) vary for the samples from a large value of 2 \times 10^{18} cm^{-2} to a low value of 6 \times 10^{17} cm^{-2}. This variation in \( p_s \) with barrier composition again can only be explained by the assumption that the 2DHG is polarisation-induced. Also, mean values for hole mobilities are listed in Table I. The value of 30 cm^{2}/Vs for sample C marks the highest one reported to date [9] at such high carrier density.

Finally, transfer characteristics of transistors with a gate length of 1 \mu m are shown in Fig. 3. Sample E exhibits the lowest drain current in on- and off-state. Additionally, the pinch-off voltage \( V_P \) is slightly below 0 V, indicating clear enhancement mode behaviour. With increasing Al content in the barrier, \( V_P \) moves towards more positive values.

![Figure 2: Profile of Mg concentration obtained by SIMS. After [8].](image)

![Figure 3: Transfer characteristics in semi-logarithmic scale. After [9].](image)

This effect once again proves the presence of a polarisation-induced 2DHG. In addition, the on- and off-current rise in the same manner. While for sample C, D and E, a steep subthreshold slope is observed, sample A and B show less ideal behaviour. The results shown here demonstrate that polarization engineering possible in n-channel devices can also be performed in p-channel device with very similar results. Owing to the band alignment, very large positive values for \( V_D \) are prevented, allowing easier fabrication of e-mode devices [9].

In summary, the growth and the characterisation of epitaxial layer stacks suitable for p-channel devices have been discussed. It has been demonstrated that for a successful formation of a 2DHG, Mg doping is necessary and that the 2DHG is formed by a polarisation difference at a GaN/AlGaN interface. The amount of Mg in the structure has been analysed by SIMS and the exact layer compositions by RBS. With transistors processed on the layer stacks, proper FET operation has been validated and polarization engineering has been proven to be possible in p-channel devices.

Financial support by the DFG is acknowledged.

### Table 1: Sample overview with composition, carrier densities and mobilities extracted by Hall and van der Pouw measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Barrier Composition</th>
<th>( p_s ) (10^{18} cm^{-2})</th>
<th>( \mu ) (cm^{2}/Vs)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Al_{0.6}GaN/Al_{0.4}N</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>Al_{0.5}GaN/Al_{0.5}N</td>
<td>9.8</td>
<td>19</td>
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<tr>
<td>C</td>
<td>Al_{0.3}GaN/Al_{0.7}N</td>
<td>2.2</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>Al_{0.2}GaN/Al_{0.8}N</td>
<td>1.2</td>
<td>29</td>
</tr>
<tr>
<td>E</td>
<td>Al_{0.1}GaN/Al_{0.9}N</td>
<td>0.6</td>
<td>23</td>
</tr>
<tr>
<td>F</td>
<td>No barrier</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>As &quot;B&quot;, no p-doping</td>
<td>-</td>
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Resistance and dopant profiling along freestanding GaAs nanowires

S. Korte\textsuperscript{1}, M. Steidl\textsuperscript{2}, W. Prost\textsuperscript{3}, V. Cherepanov\textsuperscript{1}, B. Voigtländer\textsuperscript{1}, W. Zhao\textsuperscript{2}, P. Kleinschmidt\textsuperscript{2}, and T. Hannappel\textsuperscript{2}

\textsuperscript{1}Peter Grünberg Institut-3, Forschungszentrum Jülich, Germany
\textsuperscript{2}Institute for Physics, Photovoltaics Group, Technische Universität Ilmenau, Germany
\textsuperscript{3}CeNIDE and Center for Semiconductor Technology and Optoelectronics, University of Duisburg-Essen, Germany

Resistance profiles along as-grown GaAs nanowires (NWs) were measured with a multi-tip scanning tunneling microscope used as a nanoprobe. The NWs were grown in the vapor-liquid-solid growth mode in a two-temperature-step mode and doped with Zn. Using a transport model, the resistance profile was converted to a dopant profile. The dopant distribution along the NWs was found to correlate with the temperature during different phases of NW growth. The NW base grown at higher temperature exhibits a decreased dopant concentration. Mechanical stress by intentional bending of a NW was shown not to influence nanowire conductance.

III-V nanowires could form the basis of future nanoscale electronic and optoelectronic devices. For the fabrication of novel high performance NW devices a precise control of doping density and doping profile is indispensable. However, a precise doping control is often difficult to obtain. For instance the growth of NWs can require procedures such as two-step growth, using first high temperature to initiate straight, epitaxial growth, and subsequently lower temperature to obtain untapered wires without twin defects [1]. This two-step growth process with varying temperatures is expected to influence dopant incorporation into the NWs strongly. In this work we use a multi tip STM as nanoprobe to contact as-grown, freestanding NWs, as shown in Fig. 1(a) and (b). This enabled us to measure a continuous resistance profile and, subsequently, to obtain the dopant profile along the length of a wire using resistance model calculations. We were also able to use a nanoprobe tip to bend a freestanding NW and measure its resistance in the presence of mechanical stress.

GaAs NWs as the ones shown in Fig. 1(a) were grown on \textit{n}-type GaP(111)B substrates by metal-organic vapor phase epitaxy (MOVPE) in an AIX200 RF system using monodisperse Au-particles as growth seeds as described in [2]. Prior to the NW growth diethyl zinc (DEZn) was offered at 450°C for 4 min to pre-saturate the Au-particle with Zn. The NW growth was carried out with trimethyl gallium (TMGa) and tertiary butyl arsine (TBAs) at a V/III ratio of 2.5 in two temperature steps [1]. The DEZn flow was kept constant resulting in a dopant to TMGa (II/III ratio) of 0.002. Initially the temperature was kept at 450°C for 3 min, permitting the beginning of the growth of straight, vertically aligned NWs. To reduce tapering and enhance the crystallographic quality of the NWs, the temperature was then lowered to 400°C, and growth took place for another 30 min, resulting in an average NW length of 8.2 µm.

A home-built coaxial beetle-type multtip STM [3] in combination with an SEM column was used to conduct four point electrical measurements on the as-grown NWs. The sample was tilted by 45°, so that the NWs could be observed by SEM and three electrochemically etched tungsten tips could be brought into contact with the same NW (Fig. 1(a) and (b)). The n-GaP substrate is used as additional fourth contact to the NW allowing for four-point electrical measurements to evaluate the conductance of the NW without the influence of contact resistances. Tip 1 contacted a NW at the Au seed particle on top, in order to inject and measure the electrical current \( I \) through the NW into the sample. Due to the \( p-n \) junction between \( p \)-doped NW and \( n \)-doped substrate, a measurable current flows in forward direction, only (Fig. 1(c)). During the four point measurements tips 2 and 3 contacted the NW along its length and measured the potentials \( V_2 \) and \( V_3 \) and thus the voltage drop \( V_{23} = V_2 - V_3 \) that occurred in between the contact points along the NW (Fig. 1(b) and Fig. 2(a)). From the slope of the resulting \( I \) versus \( V_{23} \) curves, the
resistance $R_{23}$ of the NW segment between the voltage probe tips was calculated by linear fit.

The measured variation of the resistance profile along the NW is attributed to a variation of dopant density $N_d$ along the wire. Since the resistance $R_{23}$ increases almost linearly both in the NW part above 2.5 µm grown at 400°C and also in the base, below 1.2 µm, grown at 450°C, we assume a constant dopant concentration in both regions (Fig. 2(b), blue line). Those parts can be described with a model (see [2]) using dopant concentrations of $N_d_{400°C} = 8 \times 10^{17}$ cm$^{-3}$ and $N_d_{450°C} = 2 \times 10^{18}$ cm$^{-3}$.

The low Zn-incorporation at 450°C can be explained by an improved pyrolysis yield of TMGa compared to 400°C, decreasing the effective II/III ratio [2]. Assuming a linear increase of $N_d$ in between, the calculated resistance profile (red line in Fig. 2(b)) exhibits very good agreement to the measured data (points). These constant doping concentrations differ from doping gradients over 10 µm found by Gutsche et al. [4]. We reduced these gradients by saturating the Au-particles with Zn dopant before NW growth.

The measured variation of the resistance profile along the NW is attributed to a variation of dopant density $N_d$ along the wire. Since the resistance $R_{23}$ increases almost linearly both in the NW part above 2.5 µm grown at 400°C and also in the base, below 1.2 µm, grown at 450°C, we assume a constant dopant concentration in both regions (Fig. 2(b), blue line). Those parts can be described with a model (see [2]) using dopant concentrations of $N_d_{400°C} = 8 \times 10^{17}$ cm$^{-3}$ and $N_d_{450°C} = 2 \times 10^{18}$ cm$^{-3}$.

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Epitaxy and Photoluminescence Studies on High Quality GeSn Layers with Sn Concentrations up to 13 at.%

S. Wirths\textsuperscript{1}, D. Stange\textsuperscript{1}, N. von den Driesch\textsuperscript{1}, T. Soica\textsuperscript{1}, A. T. Tiedemann\textsuperscript{1}, G. Mussler\textsuperscript{1}, U. Breuer\textsuperscript{2}, D. Grützmacher\textsuperscript{1}, S. Mantl\textsuperscript{1}, and D. Buca\textsuperscript{1}

\textsuperscript{1} Peter Grünberg Institut-9, PGI-9-IT, Forschungszentrum Jülich, Germany
\textsuperscript{2} Central Division of Analytical Chemistry (ZCH), Forschungszentrum Jülich, Germany

In order to reduce the power consumption of future CMOS technology optical interconnects are known to be one of the most promising alternatives to copper wires for data transfer in the mm-range. Especially, group IV semiconductors are highly desired to be employed for such applications due to their simple CMOS integration. Unfortunately, column-IV materials exhibit poor light emitting properties. Due to the small energy difference between $\Gamma$- and L-valley in Ge several approaches have been investigated recently to improve its efficiency in terms of light emitting such as tensile strain and/or heavy n-type doping \cite{1}. In the last decade another technique emerges more and more, i.e. alloying Ge with Sn. The higher the substitutional Sn concentration in the Ge lattice the smaller the energy difference between the $\Gamma$- and L-valley. However, the epitaxial growth of high quality GeSn is challenging due to the low solid solubility of Sn in Ge (<1\% \cite{2}) and the huge lattice constant mismatch (15\%). Here, we present structural and optical characterization of high Sn content GeSn binaries that are suitable for group IV photonic devices.

The GeSn layers under investigation have been grown using a 200 mm reduced pressure chemical vapor deposition (RPCVD) tool with showerhead technology. The special design in combination with the developed growth process enables high quality Si-Ge-Sn epitaxy at very low growth temperatures \cite{3–5}. We use Ge\textsubscript{2}H\textsubscript{6} and SnCl\textsubscript{4} as precursors which are led into the reactor chamber via N\textsubscript{2} carrier gas. A set of GeSn epilayers with Sn concentrations ranging between 8 at.\% and 13 at.\% have been grown pseudomorphically and partially relaxed on high quality Ge-buffered Si(100) wafer (Ge-VS) \cite{4}. X-ray diffraction (XRD), Rutherford Spectrometry (RBS) and Transmission Electron Microscopy (TEM) have been applied to study the single crystalline quality and the strain relaxation mechanism of the grown layers. To determine the incorporated strain Reciprocal Space Maps (RSM) have been carried out. The optical quality and the ability to emit light were investigated by room temperature Photoluminescence. The PL peak shift with the Sn content and strain is compared to theoretical band structure calculations. Finally, 8x8 k.p electronic band structure calculations are used to investigate the optical gain as function of the injected carriers as well as of the doping level.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Sketch of the electronic band structure of GeSn with increasing Sn alloy concentration towards indirect to direct transition. For sufficiently high Sn concentrations the $\Gamma$-valley lies energetically below the L-valley.}
\end{figure}

In Figure 2a 0/2θ-scans of three 30 nm GeSn layers are presented. Well-shaped GeSn along with Si and Ge peaks are observed. The well-defined thickness fringes around the GeSn peaks indicate high single crystalline quality growth. The Sn concentrations are found by fitting the 0/2θ-scans. Since Sn has a larger cubic lattice constant compared to Ge, the GeSn peaks for layers exhibiting larger Sn concentrations grown at lower growth temperatures shift towards smaller angles due to the larger out-of-plane lattice constant. To determine the latter as well as the in-plane lattice constant RSMs of the GeSn/Ge/Si(100) heterostructures have been carried out. It has been found that the peak of the about 2.5 µm thick Ge buffer lies below the cubic lattice line indicating a slight tensile strain of 0.16 \% whereas the peak of a Ge\textsubscript{0.87}Sn\textsubscript{0.13} layer is on the pseudomorphic line proving pseudomorphic growth. By using the bowing corrected Vegards law \cite{6} a large compressive strain of about -1.9 \% is obtained.
FIG. 2: θ/2θ scans for GeSn layers with 9, 12 and 13 at. % Sn. The GeSn peak shifts towards lower angles with the Sn content.

Room temperature photoluminescence (PL) measurements of these highly strained layers are presented in Fig. 3-top. Strong photoluminescence indicates high optical quality, never shown before for these high Sn concentrations. The observed oscillations in the spectra are due to Fabry-Perot (FP) resonances from the underlying Ge buffer layers. The peaks are shifted to lower energies for higher Sn concentrations according to band structure calculations. In Figure 3-bottom luminescence spectra for partially relaxed layers are shown. The Sn concentration of these layers of 8-13 at.% have been determined by RBS as well as the layer thicknesses ranging between 200 and 300 nm. RSM measurements exhibit a degree of relaxation of up 70%. Again, we observed strong luminescence at room temperature which is a proof of high crystalline quality of the GeSn alloys with a very low defect density. The small PL signal at 0.35 eV is attributed to the misfit dislocation network at the GeSn/Ge-VS, the driver of the relaxation process. The main PL peak position is further shifted to lower energies as compared to the fully strained layers owed to the lower bandgap of these relaxed layers. Relaxed GeSn layers are highly desired since the Sn concentration required for the indirect to direct bandgap transition decreases with increasing strain relaxation or inducing tensile strain [4]. Additionally, the layers thicknesses in combination with the high single crystalline quality make these GeSn/Ge heterostructures grown on Si(100) a promising material system for efficient group IV light emitters.

Gain calculations were performed for strained and relaxed GeSn layers indicating that large gain values can be obtained for low n-doping for our layers with Sn contents below 12% and no doping requirements are necessary for GeSn alloys with Sn contents above 12% and high strain relaxation where the material becomes fundamental direct bandgap semiconductor.

In conclusion, high quality GeSn layers grown on Ge-VS/Si(100) were achieved with high compressive strain values of up to -1.9 % and Sn concentrations up to 13 at.%. Room temperature luminescence indicates high optical quality for fully strained and partially relaxed layers. These findings evidence the high potential of GeSn alloys to be implemented in future active optoelectronic devices.

Contacting moderately doped Emitters of Silicon Solar Cells with Dopant Segregation During Nickel Silicidation

M. Lenz, H. Windgassen, T.M. Pletzer, and J. Knoch
Institute of Semiconductor Electronics, RWTH Aachen University, Germany

A further increase of solar cell efficiencies requires reducing recombination losses while keeping parasitic resistances and the shadowing at a minimum. In silicon solar cells recombination can be lowered by decreasing the emitter doping concentration, however, at the cost of increasing contact and sheet resistances. Here, we show that using dopant segregation during silicidation emitters with low doping concentration can be contacted and that a substantial performance improvement of silicon solar cells exhibiting such an emitter with a peak doping concentration of $6 \times 10^{18}$ cm$^{-3}$ can be obtained. Furthermore, we show that the small achievable contact resistances in principle allow a substantial reduction of the contact area. In turn this enables lowering the shadowing while at the same time decreasing the sheet resistance due to a larger number of front contacts that can be placed close to each other. Using PC1D simulations we study the solar cell performance as a function of the emitter dopant concentration estimating the achievable efficiency increase when employing dopant segregation.

The formation of the emitter of a solar cell and its contacting with a metal are crucial steps in the fabrication of a solar cell. To date, screen-printing of metallic front contacts is the most widely used process. However, at a metal-silicon interface, Fermi level pinning leads to a rather large Schottky-barrier [1,3]. Traditionally, a low specific resistance of metal-semiconductor contacts is achieved with a high doping concentration of the semiconductor at the metal-semiconductor interface. The high doping concentration yields a very thin space charge region (SCR) and thus leads to a very thin Schottky-barrier that can be tunneled through easily by charge carriers. Unfortunately, high doping concentrations result in excessive Auger recombination and free carrier absorption, substantially decreasing the efficiency of solar cells. Alternative emitter concepts such as selective emitters, where a high doping concentration exists only in the contact areas, improve the solar cell performance by reducing the effective recombination. However, the contact metallization pattern has to be aligned with respect to the highly doped regions and in any case, in ‘conventional’ metallization schemes, the emitter profile underneath the metal contacts must exhibit a very high doping concentration to ensure a low contact resistance. As a result, the doping profile cannot be optimized independent of the requirement of achieving ohmic metal-silicon contacts.

From investigations of Schottky-barrier metal-oxide-semiconductor field-effect transistors (SB-MOSFETs) it is known that during nickel silicidation a segregation of dopants occurs that allows reducing the effective Schottky-barrier height at the metal-semiconductor interface [3]. Fig. 1 a) shows a cross-section of solar cell with NiSi contacts. If the NiSi depth remains below the junction depth of the emitter, phosphorous dopants are collected during silicidation giving rise to a thin, highly doped layer around the NiSi contact. Consequently, strong band bending (cf. Fig. 1 b)) yields a strong reduction of the effective Schottky-barrier height and hence ohmic contact formation. This fact and its implication for solar cell performance, however, have so far not been investigated in photovoltaics. Here, we study dopant segregation during silicidation to realize low resistance contacts to silicon solar cells (for details see Ref. [1,2]). Almost arbitrarily doped emitters can be contacted and hence dopant segregation during nickel silicidation makes the contact formation independent of the doping profile. As a result, the doping profile of the emitter can be optimized and contacted in an inherently self-aligned manner. We show that with optimized emitter and reduced contact size up to 2.5% efficiency gain compared to standard solar cells are feasible.

![FIG. 1: Schematic cross section of a silicon solar cell a). In b) the band diagram of an emitter with (red line) and without (blue line) segregation is depicted. The segregated dopants give rise to a strongly reduced effective Schottky-barrier $\Phi_{SB}$.](image-url)

5° CZ boron doped single side polished wafers are used for the fabrication of the solar cells. After cleaning, POCl$_3$-diffusion was carried out. Subsequently, the phosphorous silicate glass
(PSG) was removed using HF solution. The samples were post annealed at 1050°C for 2h to drive-in the emitter and lower the surface peak concentration. The resulting emitter had a surface doping concentration of $N_D = 6 \times 10^{18} \text{cm}^{-3}$ and a depth of 700nm. A SiN$_x$ passivation layer was deposited using a PECVD process. Afterwards, the wafers were laser cut into 2x2cm$^2$ samples. To open the SiN$_x$ layer, a 50nm SiO$_2$ layer was sputter deposited onto the SiN$_x$, acting as an etch mask. The metallization grid was defined by lithography with a shadow mask equal to the grid design. After etching the oxide layer with a 5% buffered HF solution, the SiN$_x$ layer was opened with H$_3$PO$_4$ at a temperature of 150°C for 40min. Different Ni layers with thicknesses in a range of 8 to 80nm were then deposited by electron-beam evaporation at the front side using the same shadow mask utilized for lithography. The same Ni layer thickness was applied on the backside over the entire area to build up the back contact. By annealing the samples in a rapid thermal processing (RTP) furnace at 500°C for 30s, the Ni was completely consumed, producing a NiSi layer, ranging from approximately 10nm to 100nm in thickness. Finally, a 5µm thick Ni layer was deposited using a shadow mask in the case of the front side of the solar cells and a 1µm thick homogeneous Ni layer on the backside.

I-V curves of the resulting solar cells are shown in Fig. 2. The effect of the segregation on the series resistance and thus on the fill factor (FF) is apparent. For the 100nm NiSi sample (green curve in Fig. 2) a fill factor of 71% is achieved. A small difference to the 20nm NiSi layer (blue curve) is observable with a FF of 69%. By decreasing the seed nickel layer thickness to 5nm, leading to 10nm NiSi thickness, the fill factor further decreases to 54%. Finally, the curve in the as deposited case (i.e. 0nm NiSi (black curve)) shows a FF of 46%. Without the silicidation, i.e. without dopant segregation, no adequate ohmic contact can be realized because of the Schottky-barrier that builds up at the Ni-silicon interface due to Fermi level pinning.

Based on the ability to contact almost any emitter with NiSi contacts using dopant segregation, simulations are performed in order to explore the possible performance improvements of solar cells with optimized emitters. To analyze only the emitter performance, the basic properties of the cell are considered as being ideal. A boron doped wafer with a resistivity of 2Ωcm is assumed. The minority carrier lifetime for electrons and holes are kept constant at 50ms. Defects within the substrate are not taken into account. The surface recombination velocity of the rear contacts is chosen to a low value of 100cm/s and a boron back surface field (BSF) with a peak concentration of $5 \times 10^{19} \text{cm}^{-3}$ and a depth of 0.5µm is considered, to suppress the saturation current of the BSF as well. The segregation layer is modeled with a Gaussian shaped 10nm thin $5 \times 10^{20} \text{cm}^{-3}$ doped layer, placed directly underneath the contact; note that the chosen doping concentration and profile are consistent with experimental findings shown in Ref. [3]. To evaluate an emitter structure with segregation layer the peak dopant concentration as well as the junction depth $d_J$ of the underlying emitter are varied. The thickness and concentration of the segregation layer are kept constant.

In summary, we demonstrated that employing silicide induced segregation of phosphorous dopants allows ohmic contacts formation to lowly doped emitters of silicon solar cells. In turn this enables an optimization of the emitter dopant profile towards lowly doped emitters with larger junction depth. We showed with simulations that a further increase of the cell’s efficiency of more than 1% abs. is feasible.

**FIG. 2:** Experimental I-V characteristics of solar cells with different Ni seed layer and thus different NiSi layer thicknesses.

**FIG. 3:** Solar cell efficiencies as a function of the surface doping concentration for different junction depths $d_J$.

Fig. 3 shows simulated efficiencies as a function of surface dopant concentration together with the efficiency in the case of a solar cell with a typical selective emitter. The benefit of decreasing the emitter dopant concentration while increasing the junction depth are apparent and amount to more than 1% abs.

In summary, we demonstrated that employing silicide induced segregation of phosphorous dopants allows ohmic contacts formation to lowly doped emitters of silicon solar cells. In turn this enables an optimization of the emitter dopant profile towards lowly doped emitters with larger junction depth. We showed with simulations that a further increase of the cell’s efficiency of more than 1% abs. is feasible.

Electrical characterization of mercapto-phenylamine capped AuNP in a heterometallic nanoelectrode gap

N. Babajani¹, S. Karthäuser¹, R. Waser¹, C. Kaulen², M. Homberger², and U. Simon²

¹ Peter Grünberg Institut-7, Forschungszentrum Jülich, Germany
² Institute of Inorganic Chemistry, RWTH Aachen University, Germany

We report on hybrid electronic devices based on molecule capped nanoparticles immobilized between heterometallic nanoelectrodes forming asymmetric contacts. To study the effects that arise from the different metal-molecule contacts, gold nanoparticles capped with mercaptophenylamine have been synthesized and immobilized in the nanogap by dielectrophoresis. The resulting devices were characterized by cyclic electron-transport measurements. Thereby, we obtained distinct transport characteristics depending on small differences in the device geometry.

Here, we follow the concept to integrate nanoelements with tailored functionalities into traditional CMOS circuitry. In this connection, one major challenge is to fabricate nanodevices bearing rectifier functionality in a reliable way. According to theory, in a heterometallic nanogap bridged by a molecule capped gold nanoparticle (AuNP) unequal work functions of the metals or different transmission coefficients between the molecular anchor groups and the electrodes should result in the formation of a rectifier [1]. Hence, heterometallic nanoelectrodes are one requirement to build-up a rectifier.

Fabrication of Heterometallic Nanogaps: The heterometallic nanoelectrodes were fabricated by combining an optimized e-beam lithography (EBL) process with a self-alignment procedure to form nanogaps as small as 5 nm. First, platinum nanoelectrodes were defined by EBL in a lift-off process using a double layer resist stack and a two step development procedure [2]. The Pt-electrode and the Al-layer were deposited by an e-gun-evaporator (1 nm Ti, 13 nm Pt, 11 nm Al) and subsequently, the sample was exposed to air whereby the aluminum was oxidized. Thus, an augmented Al₂O₃-layer on top of the Pt-layer with an overhang of about 13 ± 2 nm was formed for the following self-alignment process. After lift-off the same procedure as described above for the Pt-electrodes was applied to fabricate AuPd-nanoelectrodes and subsequently, the Al₂O₃ was removed. Thus, heterometallic nanogaps were obtained with a separation between the Pt- and the AuPd-electrodes corresponding to the nanometer sized gap predefined by the Al₂O₃ hard-mask on top of the Pt-electrodes. (FIG. 1)

FIG. 1: a) Schematic of the self-alignment step using the Al₂O₃ hard mask to form the gap between the central Pt- and the AuPd-electrodes. b) SEM image of a 5 nm gap between an AuPd- and a Pt-electrode.

FIG. 2: Preparation scheme of mercaptophenylamine capped AuNP, by immobilizing citrate-AuNP on aminosilanized glass beads, subsequent addition of MPA in acidified H₂O and release of MPA-AuNP by ultrasonication.
Synthesis of 4-Mercaptophenylamine (MPA) Capped AuNP: MPA stabilized AuNP were synthesized applying a solid phase supported approach [3]. Thereby, citrate stabilized 15nm AuNP were immobilized on aminosilanized glass beads, acidified with HCl, and treated with an ethanolic solution of MPA in order to induce ligand exchange. MPA-AuNP were released from the solid support by ultrasonication and ligand exchange was completed (FIG. 2). Free citrate molecules and excess of thiol ligands were removed by repeated centrifugation and redispersion in acidified water. In order to optimize the dielectrophoretic trapping procedure of the AuNPs in the nanogaps the pH value and thereby, the degree of protonation, was systematically investigated in HEPES buffer solution [4].

Transport Measurements on MPA-AuNP Trapped within a Heterometallic Nanogap: In order to prove the impact of asymmetric molecule-metal-contacts cyclic I/U-measurements were performed on MPA-AuNP immobilized between an AuPd- and a Pt-nanoelectrode. Further, the transport mechanism was investigated by transition voltage spectroscopy (TVS) and finally the devices were analysed by SEM [4] (FIG. 3).

The obtained devices revealed low noise TVS curves with a distinct minimum. From this minimum we deduced a tunneling barrier height of $\phi_{\text{exp}} = 0.85 \pm 0.1$ eV. This value is in good agreement with literature data for tunneling barrier heights corresponding to phenylene groups ranging from 0.67 to 0.82 eV and confirms that the MPA molecules form the tunneling barrier. On the other hand it turned out that the conductivities obtained for these devices are much smaller than theoretical values calculated from the Landauer-formula. This deviation can be explained by the existence of a small vacuum gap between molecular capping layer and the electrode. To get further insight into the nature of the assumed vacuum gap and to prove, that the ligand shell of the AuNP is still intact, XPS investigations of MPA-AuNP on a Pt-surface were performed. The obtained Pt 4f, Au 4f, N 1s, C 1s core level spectra showed peaks with binding energies corresponding to the adsorption of MPA on Au, as expected. However, the O 1s core level spectrum revealed an unexpected peak attributed to electron deficient oxygen involved in hydrogen bonds to amine groups. Thus, water molecules linked to MPA by hydrogen bonds were identified. Recalculation of the conduction through the MPA-AuNP device considering additional water molecules incorporated into the ligand shell around the AuNP result in a value of 10.1 nS. This value is in astonishing agreement with the measured device conductivity (5 – 30 nS) confirming that tunneling is the relevant transport mechanism in such devices. Furthermore, the water molecules are the reason why the expected rectifier functionality arising from MPA-AuNP immobilized in heterometallic nanogaps is masked. Thus, symmetric I/U-curves (FIG. 3a) are obtained in our devices.

Summarizing, the highly reproducible fabrication of heterometallic nanogaps with gap sizes down to 5 nm was achieved. MPA-AuNP were synthesized by a new solid phase supported approach and integrated in nanogaps by dielectrophoretic trapping. I/U-measurements on the obtained devices revealed a tunneling barrier for MPA of $\phi_{\text{exp}} = 0.85 \pm 0.1$ eV, which is in good agreement with literature. The expected rectifier functionality arising from these devices caused by different transmission coefficients is masked by the water molecules incorporated into the ligand shell.

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Quantification of finite-temperature effects on adsorption geometries of π-conjugated molecules: Azobenzene on Ag(111)

G. Mercurio1, R. J. Maurer2, W. Liu3, S. Hagen4, J. Meyer2, P. Tegeder4,5, A. Tkachenko3, S. Soubatch1, K. Reuter2, and F. S. Tautz1

1 Peter Grünberg Institut-3, Forschungszentrum Jülich, Germany
2 Technische Universität München, Germany
3 Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany
4 Freie Universität Berlin, Germany
5 Ruprecht-Karls-Universität Heidelberg, Germany

The adsorption structure of the molecular switch azobenzene on Ag(111) was investigated by a combination of normal incidence x-ray standing waves (NIXSW) and dispersion-corrected density functional theory (DFT). The inclusion of nonlocal collective substrate response (screening) in the dispersion correction improves the description of dense monolayers of azobenzene, which exhibit a substantial torsion of the molecule. Nevertheless, for a quantitative agreement with experiment explicit consideration of the effect of vibrational mode anharmonicity on the adsorption geometry is crucial.

Precise experimentally determined structures of large organic adsorbates are indispensable for the detailed understanding of their wide-ranged functionalities, but also for benchmarking ab initio electronic structure calculations. For large molecules with polarizable π-electron systems, van der Waals (vdW) interactions are substantial and may critically influence the adsorption geometry. Accounting for these interactions in ab initio calculations remains a challenge. Due to the system sizes inherent to large molecular adsorbates, efficient semiempirical dispersion correction schemes to density functional theory (SEDC-DFT) are particularly promising. With SEDC-DFT the accuracy increases to approximately 0.1 Å for the predicted adsorption heights [1]. At this level of accuracy, a new issue arises: Experiments for structure determination are often carried out close to room temperature, while in SEDC-DFT the ground state (at 0 K) is normally calculated and the complex internal vibrational structure of large organic adsorbates is thus neglected. We demonstrate that the inclusion of such thermal expansion effects into SEDC-DFT is indeed necessary to reach quantitative agreement between experiment and theory. Hence, benchmarking at the current level of sophistication requires the careful analysis of finite-temperature effects. Otherwise misleading conclusions with respect to the SEDC-DFT accuracy might be obtained.

Our experiments have been carried out on azobenzene [Fig. 1(a)] adsorbed at Ag(111), by the NIXSW at ESRF beamline ID32 (cf. [2] for details). Molecular vibrations are expected to influence the average geometry of the adsorbate (via vibrational mode anharmonicity) and to broaden the distribution of atoms around their average positions (via vibrational dynamics). While this will affect both the coherent position $P_C$ and the coherent fraction $F_C$ of the NIXSW signal, prevalent (harmonic) Debye-Waller theory only considers temperature effects on $F_C$. Here $P_C$ defines the average adsorption height of a species, while $F_C$ quantifies the corresponding height distribution.

FIG. 1: (a) Structure formula of azobenzene (AB). (b) Side view and perspective view of AB with $\omega = 45^\circ$ and $\beta = 0^\circ$. (c) Side view and perspective view of AB with $\omega = 0^\circ$ and $\beta = 45^\circ$. $\omega$ and $\beta$ are defined as the dihedral angles CNNC and CCNN, respectively.

In the present case of AB/Ag(111), NIXSW provides $P_{C}^C = 0.27 \pm 0.02$, $P_{N}^N = 0.26 \pm 0.02$ and $F_{C}^C = 0.34 \pm 0.03$, $F_{N}^N = 0.48 \pm 0.12$ [Fig. 2], i.e. the coherent fraction of C is 29% smaller than the one of N. In our refined structure determination, we ascribe this difference to the internal geometry of AB, assuming that $F_{C}^C$ and $F_{N}^N$, the coherent fractions of individual C and N atoms, are equal. To solve the AB structure, two internal degrees of freedom are to be considered: the tilt angle $\omega$ and
the torsion angle \( \beta \) [Fig. 1], defined as dihedral angles CNNC and CCNN. Requiring \( F_c^N = F_c^C \) and constructing the molecular geometry such that the measured values for \( P_{c}^{c}, F_{c}^{c}, F_{c}^{N} \) are obtained, we find an adsorption geometry with \( dN_{Ag} \) of \( 2.97\pm0.05 \) Å, \( \omega \) of \( -0.7^\circ \), and \( \beta \) of \( 17.7^\circ \) from our NIXSW data.

As a consequence of the internal distortion of the molecule, the vertical adsorption height of the azo-bridge also increases. Analysis of achieved results reveals that that our NIXSW experiment has been carried out on a structure similar to phase A [Fig. 3 (c)]. For the phase A, the vdWsurf scheme at \( 0K \) yields a height of \( dN_{Ag} = 2.81 \) Å at tilt \( \omega = 11.7^\circ \) and torsion \( \beta = 15.4^\circ \), while the TS scheme predicts \( dN_{Ag} = 3.26 \) Å, \( \omega = 7.5^\circ \), and \( \beta = 18.6^\circ \). With regard to \( \beta \), we observe a good agreement of the ground-state calculation with the experimental result (\( \beta = 17.7^\circ \)). In contrast, the calculated \( dN_{Ag} \) are 0.16 Å too small for vdWsurf and 0.29 Å too large for TS. Including the anharmonic contributions to the vibrational motion (cf. [2] for details) improves predictions of the theory. With this we obtain for the vdWsurf (TS) calculations at 210K: \( dN_{Ag}^{vdWsurf} = 2.98 \) Å (3.23 Å), \( \omega = 9.0^\circ \) (8.8\(^\circ\)), and \( \beta = 17.7^\circ \) (17.3\(^\circ\)). Driven particularly by the low-energy adsorbate-substrate stretching modes, anharmonic effects primarily affect \( dN_{Ag} \). They lift the azo-bridge in case of vdWsurf by 0.17 Å into almost perfect agreement with the measured value of \( 2.97\pm0.05 \) Å. At the same time, the larger vertical adsorption height of the azo-bridge allows the molecule to flatten out again under the influence of the van der Waals interaction with the metal (reduction of \( \omega \)) and to twist further as a result of intermolecular interactions (increase of \( \beta \)). Both tendencies bring the calculated geometry closer to experiment, although the calculated \( \omega \) remains too large. For TS, on the other hand, anharmonicity affects \( dN_{Ag} \) and \( \beta \) only mildly, because \( dN_{Ag} \) is too large even in the 0 K calculation; moreover, it has an adverse effect on \( \omega \), because it brings the molecule closer to the surface. Overall, the quality gap between vdWsurf and TS is therefore widened by the inclusion of anharmonic effects.

To check the self-consistency of the finite-temperature geometry, we simulated NIXSW results on its basis, with the aim to evaluate the influence of vibrational excitations on the coherence of the NIXSW signal. For the anharmonically corrected average structure of the molecule, the NIXSW simulation yields a \( F_c^C/F_c^N = 0.60 \) a value very close to both experiment (0.71) and the 0K structure (0.61 in vdWsurf). Most importantly, the reduction of the CF due to vibrational motion around the average structure is similar for C and N, and approximately equal to 10%, such that \( F_c^C/F_c^N \) becomes 0.63, hence closer to experiment. The nearly equal reduction of \( F_c^C \) and \( F_c^N \) due to thermal vibrations confirms a posteriori that in deriving the experimental structure we can interpret the different experimental coherent fractions as being due to static distortion.

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Calibrating atomic-scale force sensors installed at the tip apex of a scanning tunnelling microscope

G. Kichin, C. Wagner, F. S. Tautz, and R. Temirov

Peter Grünberg Institut-3, Forschungszentrum Jülich, Germany

Scanning tunnelling microscopy (STM) tips decorated with either a single carbon monoxide molecule or a single xenon atom are characterised by simultaneous force and conductance measurements using a combined low-temperature non-contact atomic force and scanning tunnelling microscope (NC-AFM/STM). It is shown that in both cases the particle decorating the tip simultaneously performs the function of an atomic-scale force sensor and transducer which couples the short-range force acting on the tip to the tunnelling conductance of the junction. On the basis of the experimental data, two distinct coupling regimes are identified; in one of them the force sensor-transducer function is calibrated quantitatively.

Almost thirty years after its invention, the technique of scanning tunnelling microscopy (STM) still experiences many exciting developments. One of them - the recently reported scanning tunnelling hydrogen microscopy (STHM) - extends the imaging capabilities of low-temperature STM by filling the junction with molecular hydrogen (H₂) [1]. As has been revealed in the latest experiments, the structural resolution produced in STHM experiments is generically induced by STM tips decorated with either single molecules (H₂, D₂, CO, CH₄) or atoms (Xe) [2]. In an attempt to identify the mechanism that induces the STHM resolution, it has been proposed that the particle decorating the STM tip functions as a combined "force sensor" and "signal transducer" [1,2,3,4,5]. The possibility to use the STM tip as a microscopic force sensor provides interesting opportunities both for high-resolution imaging and spectroscopy. However, before these opportunities can be fully exploited, it is necessary to develop a quantitative model describing the STHM imaging mechanism. Here we make an important step in this direction, presenting simultaneous force and conductance measurements on the basis of which the sensor-transducer function of the decorated STM tips is quantitatively calibrated.

For the purpose of calibrating the microscopic sensor-transducer comprised of a single particle adsorbed at the STM tip apex, we set up an experiment in which a known force is applied to the tip and the response of the junction conductance is measured. To obtain the correct calibration it is necessary to separate the effect of the force applied to the sensor from all other factors influencing the conductance. Therefore the force cannot be tuned by simply changing the tip-surface distance, because in that case the tunnelling current mostly follows the changes of the local density of states (LDOS).

**FIG 1:** Sequences of $\Delta f$ (grey) and $\frac{dI}{dV}$ (grey/green) constant height images used for the calibration. A - measured with CO-tip, B - measured with Xe tip, B,D $F(z)$ and $\frac{dI}{dV}(z)$ curves extracted from the respective images series.
Instead, we use the finding that the force acting on the tip can be tuned in the pN range by positioning the tip at a constant distance from the surface, at different locations above the backbone of a planar organic adsorbate. Using a single 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecule residing in a monolayer film adsorbed on the Au(111) surface, we tune the force acting on the tip by moving the tip at constant height above the PTCDA.

The CO-tip resolves the internal molecular structure of PTCDA in both the $\Delta f$ and $dI/dV$ channels (cf. Fig. 1a). The appearance of molecular structure resolution in the $\Delta f$ image indicates that the tip encounters the short-range Pauli repulsion acting on it from PTCDA. Indeed, the extracted $F(z)$ spectra shown in the upper panel of Fig. 1(b) confirm that upon tip approach, the repulsion above the atom increases faster than above the ring. Therefore, the value of $\Delta F(z)$ is tuned by changing the tip-surface distance and thus can be used to characterise the conductance response $dI/dV$. Upon tip approach, in the range of distances $z=2.3 \text{Å}$, the value of $\Delta F(z)$ is positive and keeps increasing as the tip approaches the surface. At the same time the $dI/dV(z)$ curves in the lower panel of Fig. 1(b) show that the value of $\Delta dI/dV(z)$ is negative and keeps decreasing. This is direct evidence for the sensor-transducer function of the CO tip that couples $F$ and $dI/dV$. Qualitatively the coupling in this range of tip surface distances is such that the junction conductance drops as the force pressing on the tip increases.

Turning to the images recorded with the Xe tip, we first of all register that its resolution of the molecular structure is worse if compared to the CO tip (cf. Fig. 1c). The reason for the poorer image resolution is two-fold: First, as becomes apparent from the extracted $F(z)$ spectra shown in the upper panel of Fig. 1(d), the Xe tip is more reactive than the CO tip; as a result, both the $\Delta F(z)$ and $\Delta dI/dV(z)$ signals come on top of a high background that makes their detection more difficult. Second, it has been observed that in comparison to the CO tip, the quality of the Xe-tip images is more sensitive to the increase of the qPlus oscillation amplitude. This could be caused by the softer tip-Xe bond and therefore stronger displacements of the Xe atom induced by the tip oscillations. Despite all the factors compromising the quality of the Xe-tip images, the extracted $F(z)$ and $dI/dV(z)$ spectra show that, similar to the CO tip, $dI/dV(z)$ and $F(z)$ are coupled.

For a quantitative analysis of the observed coupling, we plot $\Delta dI/dV(z)$ vs $\Delta F(z)$ for both types of tips. As Fig. 2 shows, upon initial approach all tips reproducibly follow a regime in which the coupling between $\Delta F(z)$ and $\Delta dI/dV$ is linear: $dI/dV(z) = \alpha F(z)$. Evaluating the coupling constants $\alpha$, we find that $\alpha_{\text{CO}} \approx 2000 \text{ S/N}$ while $\alpha_{\text{Xe}} \approx 200 \text{ S/N}$. Although the coupling has different strengths for CO and Xe tips, qualitatively it follows the same rule: The conductance of the junction decreases linearly with the increase of the force pressing on the tip.

![FIG. 2: Conductance response $\Delta dI/dV$ vs the applied force $\Delta F$. The upper (lower) panel shows spectra measured with two different CO (Xe) tips. The regime in which the response of conductance is linear is indicated by the black fitted lines. The distance at which each tip starts to deviate from the linear response regime is marked on the right.](image)

Most importantly, comparing the data collected with different tips in different experimental runs, we find that the obtained coupling constants are solely defined by the type of particle decorating the tip, but not by the tip itself. Therefore, we conclude that $\alpha_{\text{CO}}$ and $\alpha_{\text{Xe}}$ uniquely calibrate the linear regime of the CO- and Xe-based force sensors-transducers.

Nano-modified Flexible Multi-Electrode Array with an Integrated Flexible CMOS-Chip for Medical and Biological Applications

N. Winkin¹, U. Gierth², W. Mokwa¹, and M. Schneider²

¹Institute of Materials in Electrical Engineering I, RWTH Aachen University, Germany
²Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Electrochemistry, Germany

Micro-electrodes and micro-electrode arrays (MEAs) are important in a variety of medical and biological applications for recording action potentials or stimulation of neurons. In order to use them medically or biologically, it is necessary to achieve high sensitivity and resolution. To get high sensitivity, the contact between the tissue and the electrode must be very close, while to get high local resolution, a high electrode count is needed. A flexible MEA with a large area and a large number of electrodes is therefore wanted. In this work, a flexible MEA with an integrated CMOS-chip was fabricated (“Intelligent electrode”). In order to guarantee the flexibility, the CMOS-chip was thinned to a thickness of 20 µm before it was integrated. By connecting several of these “intelligent” MEAs via a bus system, the number of addressable electrodes and therefore the resolution can be increased significantly by only a few additional interconnection lines as shown in Figure 1. Furthermore, the electrode capacitance can be increased significantly by coating of the electrodes with multi-walled carbon nanotubes (MWCNT) by electrophoretic deposition (EPD).

Achieving a flexible MEA, polyimide PI-2611 was used as a carrier film. It has excellent biocompatibility and biostability [1]. First, this photo-sensitive liquid was spin-coated onto a handle wafer. After photolithography and wet chemical patterning, polyimide carrier films with a size of 7000 µm x 7000 µm x 1 µm were defined. Next, a second polyimide layer with a thickness of 25 µm was deposited, and a cavity of about 2790 µm x 2200 µm x 25 µm was created. The thinned CMOS-chip was placed into this cavity, centered, fixed, and then enclosed entirely with a third 2 µm thick layer of polyimide. This CMOS-chip was also integrated in the wireless epiretinal implant of Roessler et al. [2]. Within this third layer, contact holes were processed to connect the pads of the chip to gold electrodes by electroplating. These 2 µm thick gold electrodes were then coated with iridium oxide. It is used worldwide by many research groups, since it is adequate for the stimulation of neurons with a high charge-delivery-capacitance of more than 95 mC/cm² after electrochemical activation [3]. For electrical isolation, 3.5 µm parylene C was deposited from the gas phase. It is widely used as a coating material for medical applications [4]. Well-defined electrode openings of 100 µm in diameter were obtained afterwards by reactive dry etching. Lastly, our flexible MEA, also called “Flex-MEA” was separated from the handle wafer (Figure 2).

As mentioned before, a high sensitivity is required. To achieve this, a high effective surface area has to be built up [5]. The effective surface area of each electrode increases significantly by coating with MWCNT. Since the parylene layer of the Flex-MEA is only resistant below a temperature of...
about 125°C [6], the coating must be carried out at lower temperatures. For that reason, the EPD of MWCNT was used in the present work.

EPD is associated with particle movement in an electric field and therefore a functionalization of the MWCNT surface was required. By ultrasonic desintegration (c = 0.4 g/l), the functionalized MWCNT were dispersed in aqueous solution. After that, the Flex-MEA (working electrode) and a platinum grid (counter electrode) were located in the prepared dispersion. The electrode distance amounted to 0.25 cm and a voltage of 4.2 V was applied. The effective surface area was estimated by the capacitance of the electrochemical double layer measured by cyclic voltammetry (CV). The CVs were carried out in 0.1 M potassium chloride. A potential range from 0 – 200 mV before and 300 – 500 mV after EPD was used. A saturated silver-silver chloride electrode served as a reference, whereas platinum grid worked as counter electrode.

![Graph showing CVs of CNT coated electrode with different scanning rates.](image)

**FIG. 3.** CVs of CNT coated electrode with different scanning rates.

Figure 3 exhibits CVs at various scanning rates after the deposition of CNT on the electrode. The current behavior is nearly perfect to a typical capacitor performance. The plateau current (j_p) rises with increasing scan rate. That linear behavior leads to the ability of determining double layer capacitance by the slope of linear regression (Figure 4).

An electrophoretic deposited MWCNT layer on a gold electrode is shown in Figure 5. The shape of the layer reflects the shape of the gold electrode. The geometric area of the circular shaped coating is the same like the area of the gold electrode. An over coating effect is not visible. The determination of the double layer capacitance of the bare gold surface results to approximately 29 µF/cm². The capacitance increases to approximately 1.01 mF/cm² after the electrophoretic deposition of CNT. Consequently, the effective surface is enlarged by factor of about 35.

![Image showing electrophoretic deposited MWCNT layer on a gold electrode.](image)

**FIG. 5.** Electrophoretic deposited MWCNT layer on a gold electrode.

Other coatings of platinum and iridium oxide electrodes with MWCNT are still under investigation.

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Tuning neuron adhesion by AuNPs and backfill chemistry

P. Li1, S. H. Meffert3, S. Arumugam2, U. Simon2, A. Offenhäusser1, and D. Mayer1

1 Peter Grünberg Institute-8, Forschungszentrum Jülich, Germany
2 Institute of Inorganic Chemistry, RWTH Aachen University, Germany
3 Institute of Complex Systems-8, Forschungszentrum Jülich, Germany

Silicon wafers decorated with positively charged (aminoalkyl thiol) gold nanoparticles (AuNPs) were used as artificial neuron adhesion surface to which negatively charged glycocalyx of the cell membrane interacts. We varied the nanoparticle density on the surface and their environment by applying no backfill, 2-[methoxy(polyethylenoxy)6-9propyl] trichlororosilane (PEG), or octyltrichlorosilane (OTS) backfill. By this means, we tuned the chemical composition of both the cell adhesion ligands and surrounding matrix in nanometer scale. The viability of rat cortical neurons and maturation was investigated as a function of particle density and background composition.

Guiding of neuronal adhesion on solid surfaces is required for the investigation of fundamental aspects of neurobiology, for tissue engineering, and for numerous bioelectronic applications. A popular strategy to guide the adhesion of neurons is to locally apply neuron adhesion ligands to cell aversive surfaces. The neurons recognize the cell friendly areas on the surface and adhere in predefined patterns.

In particular, it has been observed that the positively charged domains of peptides assist the adhesion of neurons. These cationic domains interact with glycosylated proteins which are contributing to the accumulation of a net negative charge at the extracellular part of the membrane. In neurons, the polysialation of neural cell adhesion molecule (NCAM) facilitates cell migration and plasticity by regulating the repulsion between adjacent cells.[1] We exploited the electrostatic interactions between the negatively charged glycocalyx and particle associated cationic molecules to immobilize neurons on solid surfaces. However, the cell viability on such surfaces not only depends on cues that support cell adhesion but also on the matrix surrounding these cues. In particular hydrophobic molecules, protein aversive ethylene glycols, and surfaces with negative charges have been identified as suitable compounds to regulate cell adhesion without being cytotoxic.

In this study, we used a simple and efficient strategy to deposit randomly close-packed 20nm AuNPs on a solid surface from colloidal solution by electrostatic interactions between oppositely charged particles and the solid surface [2]. The density of particles on the surface can be tuned by diluting the particle solution. The AuNPs were functionalized by 11-amino-1-undecanethiol (AUT), a molecule that possesses a positive charge under neuron culture conditions. The amino-functionalized gold nanoparticle (AF-AuNP) can be considered as cationic anchor spots for glycosylated plasma membrane proteins similar to widely used cationic polyamino acids like poly(lysines), however with strongly confined size and control over density and local distribution. Samples homogeneously modified with poly-D-lysine (PDL) were used as control to evaluate the maturation of the neurons. In addition, we changed the surrounding background of the AF-AuNP to vary the chemical contrast between the particle and their environment. We investigated the influence of three common background materials: bare SiO2 which possesses a negative net-charge at neuron culture conditions, protein repellant polyethylene glycol silane molecules, and hydrophobic octyltrichlorosilane (OTS).

Since the density of surface associated particles can be tuned over large ranges, we are able to control the density of binding cues on the surface. This has a significant impact on the viability of the neurons seeded on these surfaces, Figure 1. At the lowest densities only a few particles can be
found on an area of $1 \times 1 \mu m^2$. Correspondingly, the number of particle associated binding cues is also small. Assuming a surface coverage of 5.5 AUT/\(nm^2\) on the particle surface we obtain a density of adhesion ligands of $3.1 \times 10^7$ AUT/\(\mu m^2\) on these sample surfaces. If an effective backfill, i.e. a dense coverage of the particle surrounding matrix by surface functional molecules, is applied, almost no neuron can adhere under these cell aversive surface conditions. With increasing particle density, the viability increases until it levels off at dense particle packing. We achieved a maximum particle density of about 500 AuNP/\(\mu m^2\). The final live cell density at the highest particle density is very similar for all type of backfills. From the density of AUT molecules, the surface charge density of the sample surface can be estimated. Considering only the AF-AuNP associated ligands, we obtain a surface charge density of \(24 \times 10^{-2}\) C/m². This value is about one order of magnitude higher than the surface charge density of \(15 \times 10^{-3}\) C/m² determined for HEK293 cells.[3] The difference between sample associated positive charges and negative cell surface charges suggests that an excess of positive charges is required at the sample surface to support the neuron adhesion. In fact, a particle density of about 30 AuNP/\(\mu m^2\) would be sufficient to compensate surface charge density of a cell. One possible reason for this finding might be the unequal distribution of the charges on both surfaces. In the case of AuNP, a huge number of ligands (see above) is bound to an anchor spot with a radius of 10nm. However, the Debye length is about 1nm for cell culture media which leads to an effective screening of electrostatic interactions.

On the contrary, the density of cell adhesion molecules (CAMs) on the cell membrane is in the range of 500 to several thousand per square micrometer. Due to the short Debye length under culture conditions just a small fraction of the CAMs would be able to bind to the surface if the particle density is as low as 30 AuNP/\(\mu m^2\). This suggests that a sufficient number of homogeneously distributed AuNP is required to allow for the binding of glycosylated CAMs which finally facilitate good cell viability. This is seemingly the case at 500 AuNP/\(\mu m^2\) for all types tested backfill.

Interestingly, the particle density at which the neurons manage to adhere to the surface strongly depends on the applied backfill. A relatively high number per unit area of vital neurons are observed for SiO₂ samples with low particle densities and without backfill. This indicates that the neurons manage to adhere at particle free areas of the negatively charged SiO₂ surface. Obviously, a dense coverage of the particle surrounding area is a powerful tool to tune the properties of surfaces on nanometer scale. Increasing densities of amino-functionalized nanoparticles enhance the adhesion of neurons. However, the particle associated binding ligands are increasing but not enabling the neuron adhesion if no backfill is applied. This observation has direct impact on attempts to guide neuron adhesion and neurite outgrowth. The chemical contrast between particle free and particle decorated areas is only moderate since cell adhesion cannot be prevented under these experimental conditions. By modifying the particle’s surrounding matrix surface domains, the cell adhesion can be suppressed for low particle densities but allows a healthy neuron maturation for dense particle packing. We used this knowledge to enhance the guiding efficiency of neurons on a predefined nanostructured surface.[4]

In summary, we found that the control of the composition of particle surrounding area is a powerful tool to tune the properties of surfaces on nanometer scale. Increasing densities of amino-functionalized nanoparticles enhance the adhesion of neurons. However, the particle associated binding ligands are increasing but not enabling the neuron adhesion if no backfill is applied. This observation has direct impact on attempts to guide neuron adhesion and neurite outgrowth. The chemical contrast between particle free and particle decorated areas is only moderate since cell adhesion cannot be prevented under these experimental conditions. By modifying the particle’s surrounding matrix surface domains, the cell adhesion can be suppressed for low particle densities but allows a healthy neuron maturation for dense particle packing. We used this knowledge to enhance the guiding efficiency of neurons on a predefined nanostructured surface.[4]

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Experimental and theoretical approaches towards understanding correlated neuronal activity

M. Helias, E. Torre, D. Grytskyy, M. Schulze-Kraft, M. Diesmann, and S. Grün
Institute of Neuroscience and Medicine-6, Computational and Systems Neuroscience and Institute for Advanced Simulation-6, Forschungszentrum Jülich, Germany

Massively-parallel electrophysiological data recorded in relation to behaviour are now available and provide the reference to constrain theoretical studies on network dynamics and interaction. Particular focus lies on the analysis of correlated activity within neuronal networks, for which we develop appropriate statistical tools. In theoretical studies we showed that synchronization is a means to suppress noise in neuronal networks. These results are not specific to a certain neuron model. In the context of a unified theoretical framework we were able to describe the general mechanisms resulting in correlated activities and to relate network structure (anatomy) to the emerging dynamics.

To get an understanding of cortical network processes related to motor behavior, we recorded massively parallel neuronal signals using a 100 electrode array implanted in the motor cortex while a monkey performed a reach-to-grasp task (Riehle et al., 2013). Neuronal signals in form of multiple single neuron spiking activities and local field potentials (LFPs) were recorded and analyzed in relation to motor preparation and different grasp types. The LFPs exhibit a large multi-component movement-related potential (MRP) around movement onset. The peak amplitude of each MRP component and its latency vary systematically across the cortical surface (Fig. 1A). Using a comparative mapping approach, we found that the spatio-temporal MRP structure relates the temporal profile of single neuron spiking activities and their somatosensory receptive field properties.

In addition, we explored how the spatio-temporal MRP structure relates the temporal profile of single neuron spiking activities and their somatosensory receptive field properties. The spatial representations of the LFP and the spiking activities overlapped extensively and related to the spatial arrangement of proximal and distal representations of the upper limb. In sum, we found that the precise spatio-temporal activation pattern is involved in the control of reach-to-grasp movements thereby providing new insights into the functional organization of motor cortex during reaching and object manipulation. For the detection and statistical evaluation of precise spike patterns in massively parallel spike data, we extended our previous work on frequent itemset mining serving for an optimized search and counting of synchronous spike patterns (Picado-Muino et al., 2013; Frontiers in Neuroinformatics). For testing the significance of spike patterns under avoidance of a massive multiple testing problem we pool the patterns according to their size and number of occurrences in a pattern spectrum (Torre et al., 2013). The entries of the pattern spectrum are compared to spectra generated from surrogate data generated from the original data by dithering, to implement the null-hypothesis of full independence (Fig. 2).

FIG. 1: Spatio-temporal neuronal responses in relation to movements. (A) Spike responses of individual neurons in relation to the start of the movement (switch release). (B) Amplitude distributions of the MRP components (P1, N1, P2, N2, P3) across the recording array.

FIG. 2: Pattern spectrum filtering on simulated data. Top: Raster plot of 100 parallel point processes including higher-order correlated spike patterns (A) and without (B). (C) Pattern spectrum containing the raw counts of patterns, (D) p-value spectrum generated on the basis of surrogates, and (E) significance spectrum, red color indicates significant patterns, listed in (F).
As a result, injected spike patterns that mimic assembly activity are well detected, thereby yielding a low false negative rate. However, this approach is prone to classify patterns as significant that result from chance overlaps of assembly activity and background spiking. We proposed the method of pattern set reduction to remove these false positives by conditional filtering. By employing stochastic simulations of parallel spike trains with correlated activity in form of injected spike synchrony in subsets of neurons, we demonstrate for a large range of parameter settings that the proposed analysis scheme allows us to reliably detect active assemblies in massively parallel spike trains.

The functional significance of correlated activity is still under debate. In particular it is unclear why synchronous activity in the input to a pair of neurons is required to explain the correlations observed in the data or whether shared input sources are sufficient. Available analytical approaches were unable to represent spike synchrony, preventing a thorough analysis. In a recent work (Schultze-Kraft et al, 2013) we extended the theoretical framework to pulse-coupling and investigated to what extent common inputs and synchronized spikes contribute to the correlated spiking activity of a pair of neurons, see Fig 3. We employed direct simulation and the new analytical methods based on the diffusion approximation, allowing us to introduce precisely timed correlations in the spiking activity of the synaptic inputs of a pair of integrate-and-fire model neurons. We identified two distinct regimes: In the limit of low correlation, linear perturbation theory accurately determines the correlation transmission coefficient, which is strictly smaller than unity.

In the presence of synchrony a qualitatively new picture arises, if the correlation is high: As the non-linear neuronal response becomes dominant, the output correlation exceeds the total correlation in the input. This transmission coefficient larger unity is a direct consequence of non-linear neural processing, elucidating how synchrony-coded signals can lead to noise suppression, a generic feature present in cortical networks. This finding hints at a beneficial role of synchrony for the information processing of the brain.

Theoretical results explain the correlated activity observed in the brain only if the obtained results are model-independent, rather than being peculiarities of the employed abstracted models. Currently a wide diversity of neuron models is used to investigate correlated activity in recurrent networks. In our recent work (Grytskyy et al, 2013), we present a unified theory of weak pairwise correlations in such networks. We consider the most frequently used models: the binary neuron model, the leaky integrate-and-fire model, and the Hawkes process. We show that linear approximation maps each of these models to either of two classes of linear rate models, including the Ornstein–Uhlenbeck process as a special case. The distinction between the two classes is the location of additive noise term in the rate dynamics. Both classes allow closed form analytical solutions for the covariance functions, an important experimental observable. The unified framework enables us to transfer results between models and to identify model-independent, generic mechanisms. Our approach is applicable to general network structures, suitable for the calculation of population averages and explains the class dependent differences between correlated activity in the time and the frequency domain. Moreover it shows that oscillatory activity emerging in networks with delayed inhibitory feedback is a model-invariant feature. The unified framework therefore presents a stepping stone to better understand the structure of correlated neuronal activity in the brain and presents the tools to identify the generic underlying mechanisms.

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Electron microscopy study of compositional segregation in octahedral Pt-Ni fuel-cell catalyst nanoparticles

M. Heggen\textsuperscript{1}, C. Cui\textsuperscript{2}, L. Gan\textsuperscript{2}, S. Rudi\textsuperscript{2}, and P. Strasser\textsuperscript{2}

\textsuperscript{1} Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institut-5, Forschungszentrum Jülich, Germany

\textsuperscript{2} Department of Chemistry, Technical University Berlin, Germany

Octahedral faceted PtNi alloy nanoparticles show exceptional activity for the oxygen reduction reaction at fuel cell cathodes. We uncover an unexpected compositional segregation structure across the \{111\} facets using aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Pristine Pt\textsubscript{1.5}Ni, PtNi and PtNi\textsubscript{1.5} nano octahedra feature a Pt-rich frame along their edges and corners, while their Ni atoms are preferentially segregated in their \{111\} facet region. We follow their morphological and compositional evolution in electrochemical environments and correlate this with their exceptional catalytic activity. The octahedra preferentially leach in their facet centers and evolve into “concave octahedra”. The segregation and leaching mechanisms uncovered here highlight the complexity with which shape-selective nanoalloys form and evolve under reactive conditions.

The identification of materials that can efficiently electro-catalyze oxygen remains a key challenge for the design of a number of important future electrochemical conversion and storage devices, such as conventional and regenerative fuel cells, Li-air batteries, or electrolyzers. In particular, the sluggish oxygen reduction reaction (ORR) on Pt limits the performance of low-temperature polymer electrolyte membrane fuel cells. After the discovery of the exceptionally ORR active Pt\textsubscript{3}Ni(111) surface \cite{1}, much efforts were dedicated to the synthesis and electrochemical investigation of octahedral skin Pt-Ni nanoparticles \cite{2}. Linear sweep voltammetry curves of octahedral Pt\textsubscript{1.5}Ni, PtNi and PtNi\textsubscript{1.5} nanocatalysts reveal a 6x - 10x increases in Pt mass activities relative to commercial carbon supported Pt nanoparticle electrocatalysts, the highest ever reported precious metal group mass activity value for a carbon-supported Pt alloy electrocatalysts \cite{3}.

Octahedral Pt\textsubscript{1.5}Ni, PtNi and PtNi\textsubscript{1.5} nanoparticles were prepared using a solvothermal method described in Ref \cite{2} and \cite{3}. STEM-EELS experiments were performed in a FEI Titan 80-300 and a FEI Titan 50-300 ‘PICO’ electron microscope operated at 300 and 80 kV. Both microscopes are equipped with a probe corrector (CEOS) and a high-angle annular dark field (HAADF) detector. ‘Z-Contrast’ conditions were achieved using a probe semi-angle of 25 mrad and an inner collection angle of the detector of 70 mrad. EELS spectra were recorded with a Gatan image filter Tridiem ERS and Quantum ERS system analyzing the Ni L\textsubscript{2,3} and Pt M\textsubscript{4,5}-edge. For the EELS line profile measurements, both Ni L-edge and Pt M-edge spectra were collected along ca. 20-30 points across individual nanoparticle with the acquisition time of 1-2 sec/spectrum.

Figures 1a-1c shows atomic-scale high angle annular dark field (HAADF) STEM images of the nanoparticles roughly oriented along \{110\} zone axis, clearly demonstrating the octahedral morphology. The images in Fig. 1b and 1c provide Z contrast and suggest non-uniform Ni distributions. For instance, the dark regions in the PtNi\textsubscript{1.5} nanoparticle (Fig. 1c) marked with white ellipses adjacent to the bright central region of the octahedron indicate a Ni-rich facet region. Z contrasts of PtNi octahedra (Fig. 1b) suggest Pt enriched edges and corners, adjacent to a Ni-rich facet region.
To further evidence metal segregation, electron energy loss spectroscopy (EELS) line analysis was applied. As shown in Figs. 2d-2f, the Pt and Ni composition distributions were studied in octahedral particles oriented along <100> zone axes (see insets). Line scans along <110> direction started and ended at the edges, passing through the central octahedron axis. The Pt$_{1.5}$Ni sample demonstrated nearly symmetrical Pt and Ni EELS profiles, thickness variations taken into account, however, their relative intensities showed a clear Pt enrichment in the central axis compared to the facets. Line scans in Figs. 1e and 1f show that Pt and Ni metal enrichment in axis and facets, respectively, increased further with more bulk Ni. In the Pt$_{1.5}$Ni sample, the facet Ni content was significantly larger than in the axis and facets with segregated Ni top layers of 4-7 atomic layers thickness (Fig. 1f). The uncovered metal segregation characteristics were further evidenced by the element map of PtNi$_{1.5}$s in Figs. 1g and 1h. In conclusion, the Pt$_{1.5}$Ni nano octahedra show a Pt-rich frame (corners and edges) and Ni-rich facet regions, which is schematically rendered in Fig. 1l. To get insight how the ORR activity trajectories of Pt-Ni octahedra correlate with structural, compositional and morphological changes, atomic-scale TEM/STEM/EELS studies of the activated catalysts were performed. Figure 2 shows PtNi nanoparticles after 25 voltammetric potential cycles, which indicate that Ni atoms have leached out from the (111) facets to varying degrees. The Pt$_{1.5}$Ni octahedra (Fig 2d,e) show enhanced Pt shell thickness of 5-12 atomic layers. The PtNi catalyst showed a mixed picture with areas of Ni depletion (arrows in Fig. 2a) but also with regions of higher near surface Ni content (Fig. 2b at position 0.5 nm). It is conceivable that the Pt-rich frame consisting of corners and edges can delay or even prevent massive leaching of Ni from adjacent areas. Possibly, the high Ni regions are those where the particle was connected to the support and thus remained intact. The mean shell thickness of the activated Pt-Ni catalyst was estimated to about 1-4 atomic layers, clearly thinner than that of the Pt$_{1.5}$Ni. The HRTEM image in Fig. 2c provided unique direct insight into how the octahedral (111) facets transform during the electrochemical activation. Only the facet centers showed preferential leaching, creating concave steps near the center of the facet. This is consistent with the Ni enrichment pattern found in the pristine materials. The most striking morphological and structural transformation, however, was observed for the activated PtNi$_{1.5}$ catalyst in the STEM image of Fig. 2f. It shows various activated particles along the <100> zone axis. Clearly visible is a well-developed dark concave shaped region inside the four quadrants spanned by the octahedral main axes. Ni leaching in the facet centers reached deep into the octahedra. This facet preferred dissolution eliminated (111) facets in favor of (100) facets. Stability tests employing 4,000 potential cycles induce a drop of the Pt mass activity of the Pt$_{1.5}$Ni, PtNi$_{1.5}$, and PtNi catalysts by 16%, 45%, and 66%, respectively. The ORR activity cannot be attributed to a loss of surface sites or bulk Ni, but again is controlled by the detailed (near) surface structure and composition. Although PtNi$_{1.5}$ demonstrated exceptional initial and activated activities, its structural transformations during cycling severely affected its activity. Microstructural investigations by HAADF-STEM and EELS revealed a dramatic morphological evolution process for the PtNi$_{1.5}$ catalyst, in which the catalyst experienced a complete disappearance of its (111) facets as well as its edges translating into dendritic nanoparticle with an orthogonal Pt rich framework [3].

![ STEM-ELS analysis of Pt$_{1.5}$Ni and PtNi octahedra after 25 potential cycles. a and b, EELS line profiles show the selective leaching of Ni in the facet region on PtNi. Relative Pt-richer corners were also observed. The STEM images in insets show the well-maintained octahedral morphology. c, HRTEM image on PtNi shows the selective leaching in the facet region. d and e, EELS line scans show the thicker Pt shell of Pt$_{1.5}$Ni relative to PtNi. These results demonstrated that after 25 potential cycles the Ni was still rich near the surface and the thickness of Pt shell in PtNi was thinner than those of Pt$_{1.5}$Ni. f, STEM image shows the formation of concave structure in PtNi$_{1.5}$, suggesting the selective leaching of Ni in the facets.](image)

In summary, we established that a Pt-rich frame (corners and edges) profile is prevalent in PtNi octahedra using HAADF-STEM in combination with EELS. We followed the lifecycle of exceptionally active electrocatalysts monitoring their catalytic activity trajectories along with their compositional, morphological and surface structural evolutions. This yielded unexpected insights in the pristine structure, the activation and degradation of these electrocatalysts. Dealing with under electrochemical conditions produced concave octahedral corrosion patterns inside the (111) facets. The collapses of the near surface alloy structure for Ni rich octahedra affects the surface adsorption of oxygen and finally depressed the ORR activity. However, our study also suggests that Pt-rich Pt-Ni octahedra exhibit relatively high and technologically relevant ORR activities in their activated state with favorable stability.

Structural and electronic properties of β-FeSi₂ nanoparticles: the role of stacking fault domains

A. Kovács¹, R. Imlau¹, P.X. Xu², C. Leidinger³, G. Bihlmayer², R.E. Dunin-Borkowski¹, R. Carius³, and M. Luysberg¹

¹ Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institut-5, Forschungszentrum Jülich, Germany
² Institute for Advanced Simulation-1 and Peter Grünberg Institut-1, Forschungszentrum Jülich, Germany
³ Institute of Energy- and Climate Research – Photovoltaics, Forschungszentrum Jülich, Germany

We use conventional and aberration-corrected transmission electron microscopy (TEM) and ab initio calculations to investigate the structural and electronic properties of β-FeSi₂ nanoparticles, which is a promising material for photovoltaic applications due to the bandgap < 1 eV and a high absorption coefficient. The nanoparticles have average sizes of ~ 20 nm, form aggregates and are prepared by gas phase synthesis. Amorphous SiOₓ shells with thicknesses of ~ 1.7 nm around β-FeSi₂ cores are identified on individual nanoparticles using electron energy-loss spectroscopy (EELS), while stacking fault domains in the nanoparticles are observed. Ab initio calculations indicate only minor changes in band structure in the faulted structure, when compared to perfect β-FeSi₂. The optical properties of imperfect β-FeSi₂ nanoparticles are therefore expected to be the same as those of the perfect structure, suggesting that β-FeSi₂ nanoparticles are suitable candidates for use in optical absorber layers in thin film solar cells.

Iron-disilicide, crystallized in the β phase (β-FeSi₂), has received considerable recent attention because of its advantageous thermoelectric and optical properties, which make it interesting for thermoelectric, as well as light-sensitive and light-emitting applications. Furthermore, β-FeSi₂ is non-toxic, consists of elements that are abundant in nature and is compatible with existing silicon-based technology [1]. Optical experiments have revealed indirect and direct band gaps of 0.78 eV and 0.84 eV, respectively. The β structure is orthorhombic with space group Cmca, has lattice parameters a=0.986 nm, b=0.779 nm and c=0.783 nm and forms in a narrow compositional range close to an Fe content of 33.3 at.%. The synthesis of β-FeSi₂ is relatively straightforward, involving the solid-state reaction of Si and Fe at elevated temperature. As lattice strain at the β-FeSi₂/Si interface changes the electronic structure and optical properties of β-FeSi₂ significantly, the synthesis of free-standing β-FeSi₂ is highly attractive for light-sensitive applications.

Here, we assess whether β-FeSi₂ NPs are suitable for use in optical absorber layers. This application requires that (i) the NPs are larger than about 15 nm to ensure sufficient optical absorption that is representative of bulk-like electronic behaviour rather than quantum confined electronic states and (ii) structural, stoichiometric compositional and electronic properties of the entire β-FeSi₂ NPs that agree with those of the bulk material. We use a wide range of advanced TEM techniques to investigate the atomic structures, morphologies and chemical compositions of individual β-FeSi₂ NPs. We determine band structures of β-FeSi₂ NPs using density functional theory (DFT) calculations, employing the generalized gradient approximation (GGA) for the exchange-correlation potential.

FIG. 1: (a) BF TEM image showing a crystalline core and amorphous shell on a β-FeSi₂ nanocrystal that was used for energy filtered TEM (EFTEM). (b) False coloured Fe L edge (green) and O K edge (red) EFTEM elemental maps recorded from the same a nanocrystal using C₀- and C₁-corrected TEM at 80 kV. (c) and (d) integrated intensity profiles of the background-subtracted (c) Fe M-edge and Si L-edge and (d) Fe L-edge and O K-edge EELS signals measured across the edge of a β-FeSi₂ NP.
β-FeSi$_2$ NPs were prepared by chemical vapour synthesis in a hot wall reactor using silane (SiH$_4$) and iron pentacarbonyl (Fe(CO)$_5$) as precursor gases. TEM studies revealed that the crystals are sintered together during synthesis into a chain-like structure and an amorphous shell is formed on their surface, as shown in Fig. 1. The crystallographic structure of the nanocrystals was confirmed to be orthorhombic β-FeSi$_2$ using electron diffraction. EELS was used to measure local variations in chemical composition within the β-FeSi$_2$ NPs and the surrounding amorphous shell. Figures 1 (a) and (b) show a BF TEM image and a corresponding Fe and O map respectively, of a β-FeSi$_2$ NP. The Fe signal is confined to the core of the crystal, while Si and significant O enrichment are observed in the shell, as shown in Fig. 1 (c and ). The presence of a small amount of Fe in the shell cannot be completely excluded. Within the margin of error, the Fe/Si ratio stays constant across the NPs, indicating a homogeneous chemical composition of the core.

The examination of HRTEM images confirmed the presence of planar defects in the β-FeSi$_2$ NPs. Inset is a digital diffractogram calculated from the image of the nanocrystal. (b) Magnified region of the HRTEM image marked in (a). The insets show simulated images of β-FeSi$_2$ viewed along (1) [021] and (2) [012]. (c) NBED pattern recorded from the nanocrystal shown in (a). Arrows mark lines of reflections visible at kH = 2n conditions.

FIG. 2: (a) HRTEM image showing planar faults in β-FeSi$_2$ NPs. Inset is a digital diffractogram calculated from the image of the nanocrystal. (b) Magnified region of the HRTEM image marked in (a). The insets show simulated images of β-FeSi$_2$, viewed along (1) [021] and (2) [012]. (c) NBED pattern recorded from the nanocrystal shown in (a). Arrows mark lines of reflections visible at kH = 2n conditions.

The influence of the experimentally observed stacking fault domains on the electronic structure of β-FeSi$_2$ was investigated by performing ab initio calculations of the band structure. After relaxation, the total energy of the most energetically favourable domain structure is ~42 meV per c(2x2) in-plane unit cell higher than that of an ideal structure with the same number of atoms. Although more complex low-energy stacking faults cannot be excluded by our calculations, the small formation energy and the experimental evidence suggest that the studied configurations are the most important ones in this material. Figure 3 displays the band structures of β-FeSi$_2$ calculated with and without domain boundaries (according to Model I), indicating only minor changes, such as a slightly larger band gap.

FIG. 3: Band structures of β-FeSi$_2$ calculated with (red) and without (black) domain boundaries. As the unit cell was doubled in the [100] direction, the bands are folded back in the FX direction.

As the NPs have an average diameter of 20 nm, the present NPs should show bulk-like electronic properties because their size exceeds the de Broglie wavelength (15.6 nm) below which quantum confinement occurs. The fact that the NPs form aggregates is not expected to result in any detrimental effect on the absorbance. Except for the amorphous shell, no indications of compositional variations within or at the edges of the NPs were found, either using EELS or from HRTEM studies, in which Fe and Si atomic columns were observed to extend to the edges of the crystalline particles. Hence, our β-FeSi$_2$ NPs are of high quality in terms of size, stoichiometry and phase purity and are expected to show the same optical properties as the bulk material and to be well suited for use in optical absorber layers, e.g., in photovoltaic devices.

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We investigated the alignment of block copolymer / nanoparticle blends in electric fields. Gold nanoparticles with dodecanethiol ligands (Au-DT NPs) selectively accumulated in the polystyrene domains of a symmetrical polystyrene-block-poly(2-vinyl pyridine) (PS-b-P2VP) block copolymer in thin films, and the lamellar structures aligned with their interfaces parallel to the electric field vector for blends with a nanoparticle loading of 0-10 wt.%.

The nanoparticles did not only serve as filler material but influenced the susceptibility of the polymeric domains to the electric field: domains aligned at significantly lower field strengths in blends with a higher nanoparticle fraction, and the quality of alignment increased. The time constant of alignment however increased with the nanoparticle loading, which could be explained by a higher viscosity of the samples.

The influence of electric fields on block copolymer structures has been explored for more than two decades now. Not only can morphologies with a uniaxial symmetry like lamellae and cylinders be aligned, also distortion of mesostructures, order-disorder transitions and even transformations of one morphology to another may result when electric fields are applied to phase separated block copolymers [1]. More recently, also simulations of the behavior of composite materials composed of block copolymers and nanoparticles have been performed in our group, while experimental studies on such systems were not employed yet. Here, we present the first experimental results of how addition of nanoparticles to a block copolymer alters its behavior in electric fields [2,3].

The material under investigation consists of a PS-b-P2VP block copolymer (PS weight fraction 0.54, polydispersity 1.05, $M_w = 99$ kg mol$^{-1}$) and various amounts of Au-DT NPs ($1.6 \pm 0.6$ nm in core diameter) between 0wt.% and 10wt% respective to the polymer. Thin films as prepared from toluene solution were studied. In order to apply homogeneous electric fields in-plane to the composite films, specially designed glass substrates with lithographically pre-fabricated planar gold electrodes were used. The alignment experiments were performed during toluene vapor annealing, and the resulting structures were investigated ex situ by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM) and in situ using small angle X-ray scattering (SAXS).

Due to the hydrophobic ligands of the nanoparticles, they are selectively enriched in the polystyrene domains of PS-b-P2VP and form clusters within this block. Films that are exposed to electric fields of 10 V μm$^{-1}$ during toluene vapor annealing in a saturated atmosphere for 60 to 90 min show preferentially aligned striped patterns (lamellar block copolymer morphology) with the interfaces parallel to the electric field in AFM images or TEM micrographs (cf. Fig. 1 and [3]). In this figure, films that were annealed in the presence of an electric field (Fig. 1b,d) are compared to such that were annealed without field (Fig. 1a,c), and Fourier transforms (insets in Fig. 1) confirm preferential alignment at the film surface as also observed in by transmission SAXS in the film interior [2].

For investigating the minimum field strength that is necessary for structures to align after treatment in solvent vapor and electric field, we performed experiments on substrates with electrodes with a wedge-shaped geometry. Applying a constant voltage to the electrodes will lead to a gradient field over the length of several millimeters. This enabled us to scan different field strengths within a single experiment and hence eliminate possible
errors caused by changing experimental conditions.

FIG. 2: Threshold electric field strength for alignment of PS-b-P2VP / gold nanoparticle composite films as a function of the nanoparticle fraction in the composite. Reproduced with permission from [3]. Copyright 2013, Wiley.

Since the electric field strength gradient is very shallow, the field strength within the area of an AFM image can be considered constant and can be calculated from the electrode spacing at the investigated position. A comparison of AFM images and their Fourier transforms taken at different spots within the gradient gap between the electrodes shows the transition of randomly oriented to preferentially oriented domains at low and high field strength, respectively [3]. The field strength at the position where first aligned structures are observed is denoted critical field strength $E_c$. Figure 2 shows the trend of this critical field strength with nanoparticle loading in the composite. A clear trend of lower $E_c$ with increasing nanoparticle loading is observable.

The kinetics of alignment was investigated by means of in situ SAXS. Thick block copolymer or composite films were annealed in toluene vapor with and without electric field, and in regular time steps SAXS patterns were measured. From the orientation of spots with high intensity, the order parameter $P_2$ was calculated which is 0 for randomly oriented domains and -0.5 for perfect alignment parallel to the electric field [3]. The average domain spacing $D$ was also calculated from the scattering vector for every time step. Figure 3 shows the developing of $P_2$ and $D$ with continuing annealing in the presence of the field.

First order kinetic fits for $P_2$ with time yield the time constant $\tau$ of alignment and the potential order parameter after infinite experimental duration $P_{2,\infty}$. Figure 4 summarizes the results for composites with different nanoparticle loading.

The experiments clearly indicate that the more nanoparticles are incorporated in the polymer, the weaker the field must be at least to yield aligned structures. Similarly, application of the same field strength leads to better alignment compared to neat block copolymers. This can be understood as a result of increasing dielectric contrast between the blocks due to selective nanoparticle incorporation and hence higher susceptibility to electric fields. The slower kinetics may be caused by increasing viscosity of composite films compared to pristine block copolymers.

FIG. 3: Order parameter $P_2$ (a) and average domain spacing $D$ (b) as functions of experiment time for a pure PS-b-P2VP film (hollow circles) and for a composite film containing 3 wt.% Au-DT NPs in PS-b-P2VP (filled circles). The vertical lines mark the starting point of the exponential fit functions. Reproduced with permission from [2]. Copyright 2013, American Chemical Society.

FIG. 4: Time constants $\tau$ (black filled squares, left axis of ordinates) and asymptotic orientational order parameter $P_{2,\infty}$ (red hollow circles, right axis of ordinates) of the exponential fit functions. Reproduced with permission [2]. Copyright 2013, American Chemical Society.

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Single-shot correlation spectroscopy for characterizing qubit dephasing

T. Fink and H. Bluhm
II. Physikalisches Institut, RWTH Aachen University, Germany

Understanding how qubits lose their phase coherence is important for improving their performance for quantum information processing. A key factor is the dynamics of the environment seen by the qubit. We propose a new technique to experimentally characterize these dynamics and consider its application to the nuclear spin bath of electron spin qubits in GaAs quantum dots. The main idea is to correlate single-shot readout signals of subsequent initialization-evolution-measurement cycles. This technique can probe a larger frequency range than established alternatives [1]. It is also useful to detect the quantum backaction of the qubit on its environment [2].

Pulse sequences like Hahn’s spin echo, CPMG, concatenated or Uhrig dynamical decoupling [3] are well known to reduce the decoherence of a qubit. They can also be used for noise spectroscopy by observing the dependence of qubit coherence on the evolution time. However, such pulse sequence based noise spectroscopy is subject to certain limitations. For a given sequence, the frequency region over which this technique is sensitive is proportional to the inverse evolution time, but longer durations also increase the total decoherence. This relation makes it hard to probe low frequency noise: by the time the frequency region of interest is accessible, complete dephasing of the qubit leaves no measurement contrast. This problem may be circumvented to some extent by adding more pulses, but this strategy will eventually be limited by π-pulse errors and the energy relaxation time of the qubit. We propose an alternative method for determining the noise spectrum over a broad frequency range without requiring many π-pulses.

It is based on correlating (near) single-shot free induction decay (FID) measurements. A typical measurement cycle is depicted in Fig. 1A and consists of initializing a x eigenstate, performing a free evolution under the influence of the noise process for time \( \tau \), a projective measurement of the final state, and repeating this process after a delay time \( \Delta t \). Averaging over many repetitions allows for computing the correlation between measurements as a function of \( \Delta t \).

We consider pure dephasing, described by a Hamiltonian

\[
H = \frac{\hbar}{2} \left[ \Omega + \beta(t) \right] \hat{\sigma}_2,
\]

where \( \Omega \) is the qubit energy splitting and \( \beta(t) \) represents a classical, Gaussian noise process with \( \langle \beta(t) \rangle = 0 \). We find that the relevant term in the autocorrelation function of the single shot outcomes is given by

\[
\langle \mathcal{P}(\tau, t) \mathcal{P}(\tau, t + \Delta t) \rangle = \frac{1}{2} e^{-\frac{1}{2} \chi^2(\tau \Delta t)},
\]

\[
\chi^2(\tau, \Delta t) = 16 \int_0^\infty \frac{d\omega}{\pi} S_{\beta}(\omega) \frac{\sin^2 \left( \frac{\omega \tau}{2} \right) \sin^2 \left( \frac{\omega \Delta t}{2} \right)}{\omega^2}
\]

\( \chi^2(\tau, \Delta t) \) is a two-parameter generalization of the corresponding result for a simple spin echo. By varying the delay time \( \Delta t \), one can shift the weight of the filter function in \( \chi^2(\tau, \Delta t) \) in the frequency domain and thus tune the highest sensitivity to the frequency range of interest. Note that for \( \omega \tau \ll 2 \), the evolution time controls the gain factor and thus the overall sensitivity. The ability to adjust both the sensitivity’s overall magnitude and position of the support of our method. Suitable choice of evolution and delay time allows for maintaining a good measurement contrast when investigating spectral content over a wide frequency range.

As an example, we consider electron spin qubits in gate-defined GaAs quantum dots. For these qubits, the hyperfine interaction couples each electron spin to \( \sim 10^4 \) nuclear spins, leading to \( \beta(t) = \frac{g_B}{\hbar} B_L(t) \), where \( B_L \) is the hyperfine-induced effective magnetic field seen by the electron. The temporal fluctuations of \( B_L \) are due to spin diffusion processes that enable distant
nuclear spins to exchange polarization. Treating these processes as classical diffusion leads to a noise spectrum proportional to $\omega^4$, but microscopic theory [4] and experiments imply that the $\omega^3$ dependence is only valid below about 10 kHz. We find that our method is well suited to detect a high frequency cutoff. Fig. 1B shows corresponding results for a model spectrum of the form

$$S_{\text{mix}}(\omega) = \frac{S_0}{1 + \left(\frac{\omega}{\omega_0}\right)^2} \times \exp \left[-\left(\frac{\omega}{\omega_0}\right)^2\right].$$

So far, we have treated the qubit’s environment as a classical fluctuating field with Gaussian statistics, which enables us to express measurement results and qubit dephasing in terms of the noise spectral density. A much more general approach is to use a fully quantum mechanical description. However, the solution of the resulting quantum many-body problem is usually very challenging. It is thus of great interest under what conditions the classical description is a good approximation to a full quantum model. Broadly speaking, does a bath behave quantum mechanically or classically? Introducing an additional evolution stage between the two measurement cycles of the above scheme (Fig. 2A) leads to a qualitative experimental discrimination of these regimes. A change of the correlations due to the backaction of the intermediate interaction implies the breakdown of the classical description. Such a backaction is required by the uncertainty relation whenever the Hamiltonians governing the intermediate and the measurement interaction periods do not commute. Thus, the proposed experiment can also verify fundamental predictions of quantum mechanics.

As a concrete and practically relevant example, we again consider an electron spin qubit in a GaAs quantum dot. Given the mesoscopic nature of its nuclear spin bath, the question whether quantum effects can be observed is particularly pertinent. While quantum models have been considered in detail [4], all experiments to date can be explained in a classical picture of the bath [5, 6]. Here we find that the backaction should be observable with established experimental methods. One practically convenient approach to generating non-commuting interaction Hamiltonians is to apply different pulse sequences to the electrons.

For a FID experiment, the final qubit measurement predominantly probes the nuclear polarization along the external field direction. In a spin echo (SE) experiment, a $\pi$-pulse applied to the qubit eliminates any constant interaction with this longitudinal field. However, second order terms make the SE decay sensitive to the time-dependent transverse Overhauser field components that oscillate because of the relative Larmor precession of the different isotopes in the system. Implementing the two outer evolutions of Fig. 2A as a SE and the intermediate evolution as a FID effectively creates the required non-commuting evolutions. Differences observed between the SE-FID-SE and the SE-SE-SE schemes will then allow one to directly identify any backaction. We make use of a semiclassical approach [7] to calculate the autocorrelation function. The results depicted in Fig. 2B show revivals whenever the three nuclear species have the same relative orientation during both measurements, i.e., a multiple of the relative precession periods has elapsed. Turning on the backaction by introducing the intermediate FID leads to a clear suppression of the correlation revivals. This is due to the Knight shift experienced by the nuclei during the FID which changes the relative phase of the Larmor precessions.

Further experimental and theoretical work shows that the same technique can also reveal the nuclear Larmor precession and its dephasing when probing qubit transitions driven by transverse nuclear fields.

Hall Effect Gyrators and Circulators

G. Viola\textsuperscript{1} and D. DiVincenzo\textsuperscript{1,2}
\textsuperscript{1} Institute for Quantum Information, RWTH Aachen University, Germany
\textsuperscript{2} Peter Grünberg Institut-2, Forschungszentrum Jülich, Germany

The electronic circulator, and its close relative the gyrator, are invaluable tools for noise management and signal routing in the current generation of low-temperature microwave systems for the implementation of new quantum technologies. Capacitive coupling to a Hall conductor has promise for achieving good circulator and gyrator functionality with device dimensions far smaller than the a.c. wavelength. We formulate a classical Ohm-Hall analysis for calculating the properties of such a device. An experiment is proposed to achieve GHz-band gyration in millimetre (and smaller) scale structures employing either semiconductor heterostructure or graphene Hall conductors.

The essence of the three-port circulator is its non-reciprocal routing of signals: electromagnetic radiation is passed cyclically from one port to its neighbor – radiation in at port one goes out at port two, in at two goes out at three, and in at three goes out at one, see Fig. 1. The $S$ matrix describing the circulator is simply

$$S = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$  \hline

A typical present-day experiment involving just a single superconducting qubit requires no fewer than four circulators for the proper management of signals used to do high-fidelity, rapid measurements on the qubit. (A new three-qubit experiment is now reported with no fewer than eleven circulators!) While highly reliable and reasonably close to ideal in their designed frequency band of operation, they are quite bulky. It is well known how to achieve miniaturization of the circulator function to far below wavelength scale using operational amplifier circuits. But even if such electronic circuits could work at cryogenic temperatures, their power dissipation and noise performance would be unacceptable for current applications. A group at the Bell Telephone research laboratories took up experiments in the 1950s to realise gyration using the Hall effect (Fig. 2).

But gyration can only be poorly approximated by this device due to loss. We will now state a new boundary condition that is appropriate for the case of a segment of boundary of a Hall conductor forming one side of a capacitive coupling as shown in Fig. 3. Such a capacitor will be characterised by having a capacitance per unit perimeter length $c(s)$. While $c(s)$ should be viewed purely as a phenomenological capacitance function, it will be important that this function incorporate the full electrochemical capacitance to the Hall material, including the quantum capacitance. We consider the external capacitor electrode to be a good conductor, and thus all at a single potential $F$. If at point $s$ on the perimeter the potential at the edge of the Hall conductor is $V(s)$, then the displacement current density $j_D(s)$ at that point of the capacitor, equal to the current density inside the Hall material directed normal to the edge $\hat{n} \cdot j(s)$, is given by the ordinary capacitance equation

$$\hat{n} \cdot j(s,t) = j_D(s,t) = c(s) \frac{d}{dt}(F(t) - V(s,t)).$$  \hline

The normal current is proportional to the rotated projection of the field gradient:

$$\hat{n} \cdot j(s,t) = -\sigma \vec{n} \cdot \nabla V(s,t) = c(s) \frac{d}{dt}(F(t) - V(s,t)).$$  \hline

We may write this equation in the frequency domain, giving our final boundary-condition equation:

$$-\sigma \vec{n} \cdot \nabla V(s,\omega) = i\omega c(s)(F(\omega) - V(s,\omega)).$$  \hline

While this is a perfectly well-posed mixed, inhomogeneous boundary condition for the Laplace equation, we are not aware that it has been previously examined. The problem of finding the
two-port response, e.g., the admittance matrix $Y$ (or $Z$ or $S$), is now straightforwardly posed: given a geometry as in Fig. 3, we identify four terminal segments $T_{1,1}$ and $T_{2,2}$ and four uncontacted, insulating segments $U_{1,1}$ and $U_{2,2}$. There is no capacitance in the $U$ regions. $c(s)$ will be nonzero along the $T$ segments. Solving the field problem as a function of $\omega$ gives normal boundary currents $\hat{n} \cdot \mathbf{j}(s, \omega) = -\sigma \hat{n} \cdot \nabla V(s, \omega)$; integrating gives the terminal currents

$$I_i(\omega) = \int_{\mathcal{S}} \hat{n} \cdot \mathbf{j}(s, \omega) ds = -\sigma \int_{\mathcal{S}} \hat{n} \cdot \nabla V(s, t) ds.$$  

(5)

These terminal currents are linear functions of the terminal potentials:

$$I_i(\omega) = \sum_{j=1,1,2} y_{ij} V'_j.$$  

(6)

The coefficients in this equation are admittances, but one further calculation is needed to obtain the two-port admittance matrix $Y$ from them:

$$I_1 = Y_{11}(V'_1 - V'_2) + Y_{12}(V_2 - V'_2),$$

$$I_2 = Y_{21}(V'_1 - V'_2) + Y_{22}(V'_2 - V'_2),$$  

(7)

thus defining the $2 \times 2$ port admittance matrix $Y$.

We now return to the four terminal device, revisiting the approach of Mason et al. (Fig. 2), with ohmic contacts replaced by capacitive contacts (Fig. 4). For the case of uniform capacitance, $c(s) = \text{const.}$, and four equal contact capacitors with capacitance $C_i$, the exact solution for the two-port response matrices is elementary. The admittance is

$$Y_{2p}(\omega) = \frac{1}{\sigma} \begin{pmatrix} \tan \frac{\omega C_i}{\sigma} & -1 + \sec \frac{\omega C_i}{\sigma} \\ -\sec \frac{\omega C_i}{\sigma} & \tan \frac{\omega C_i}{\sigma} \end{pmatrix},$$  

(8)

which when inverted gives the two-port impedance

$$Z_{2p}(\omega) = \frac{1}{\sigma} \begin{pmatrix} -i \cot \frac{\omega C_i}{2\sigma} & -1 \\ -i \cot \frac{\omega C_i}{2\sigma} & 1 \end{pmatrix}.$$  

(9)

Note that $Y$ and $Z$ satisfy the conditions for multiport lossless response, which are that the imaginary part of the matrix be symmetric and an odd function of frequency, while the real part is antisymmetric and an even function of frequency.
Conductance scaling in Kondo correlated quantum dots: role of level asymmetry and charging energy

L. Merker1, T. A. Costi1, E. Muñoz2, and S. Kirchner3

1 Peter Grünberg Institut-2 and Institute for Advanced Simulation-3, Forschungszentrum Jülich, Germany
2 Facultad de Física, Pontificia Universidad Católica de Chile, Santiago, Chile
3 Max Planck Institute for the Physics of Complex Systems, Dresden, Germany

The low temperature electrical conductance through correlated quantum dots provides a sensitive probe of the physics (e.g., of Fermi-liquid versus non-Fermi-liquid behavior) of such systems. Here, we investigate the role of level asymmetry (gate voltage) and local Coulomb repulsion (charging energy) on the low-temperature and low-field scaling properties of the linear conductance of a quantum dot described by the single-level Anderson impurity model. Our results could be a useful guide for detailed experiments on conductance scaling in semiconductor and molecular quantum dots exhibiting the Kondo effect.

Motivated by recent experiments on conductance scaling in correlated quantum dots exhibiting the Kondo effect [1,2] we carried out a detailed study of the low-temperature and low-field scaling properties of the linear conductance of a quantum dot described by the single-level Anderson impurity model [3]. Scaling in physical properties is a hallmark of the Kondo effect [4]. Thus, a Kondo model description of a quantum dot implies that the conductance \( G(T,B) \) is a universal function of \( T/T_0 \) and \( \frac{g\mu_B B}{k_B T} \) over all temperatures \( T \) and magnetic fields \( B \) with microscopic parameters (such as the Kondo exchange \( J \)) only entering through the dynamically generated low energy scale \( T_0 \), precisely by \( \chi(0) = \frac{(g\mu_B)^2}{4k_B T_0} \), with \( g \), \( \mu_B \), \( k_B \), \( \chi(0) \) denoting the \( g \)-factor, Bohr magneton, Boltzmann’s constant and magnetic susceptibility, respectively. In particular for \( T \ll T_0 \) or \( g\mu_B B \ll k_B T_0 \) the functions \( G(T,B=0) = G(0,0)(1-c_T(T/T_0)^2) \) and \( G(T=0,B) = G(0,0)(1-c_B(g\mu_B B/k_B T)^2) \) exhibit Fermi liquid corrections about the unitary conductance \( G(0,0) = \frac{2e^2}{h} \) with deviations which are universal in the sense that the coefficients \( c_T = \pi^2/16 \) and \( c_B = \pi/16 \) are independent of microscopic details.

Actual quantum dot devices, however, have a finite charging energy, and they are more realistically described by an Anderson model depicted in Fig. 1. The finite charging energy, and the ability to change the level energy of the quantum dot with a gate voltage, allow for charge fluctuations (even in the “Kondo regime” of the quantum dot) and can give rise to deviations from the expected Kondo scaling. It is therefore of some interest to quantify the effect of increasing charge fluctuations on the values of \( c_T \) and \( c_B \).

**FIG. 1:** A strongly correlated quantum dot described by the Anderson model with charging energy \( U » \Delta \) and level energy \( \varepsilon_d \) connected to leads via tunnel barriers. The gate voltage \( V_g ~ \varepsilon_d \) allows changing occupation of the dot \( n_d \). In the singly occupied configuration, the dot has a well-defined spin \( 1/2 \) and the Coulomb blockade excitations at \( \varepsilon_d \) and \( \varepsilon_d + U \) correspond to removing or adding an electron. The coupling of the spin \( 1/2 \) to the leads results in the Kondo effect, which is manifested by the appearance of an additional many-body Kondo resonance at the Fermi level \( \varepsilon_F = 0 \) at low temperatures \( T < T_0 \). This resonance is also reflected as a zero bias anomaly in the nonlinear conductance \( dI/dV \) in experiments.

Expressed in terms of the experimentally extracted Kondo scale, \( T_K^{\text{expt}} \), from the conductance \( G(T=0,B) = G(0)/2 \), these coefficients, denoted by \( c_T^{\text{expt}} \) and \( c_B^{\text{expt}} \), are given in terms of \( c_T \), \( c_B \), and \( T_K^{\text{expt}} / T_0 \) by

\[
\begin{align*}
    c_T^{\text{expt}} &= c_T \left( \frac{T_K^{\text{expt}}}{T_0} \right)^2, \\
    c_B^{\text{expt}} &= c_B \left( \frac{T_K^{\text{expt}}}{T_0} \right)^2.
\end{align*}
\]

Here, we shall compute these together with the ratio \( T_K^{\text{expt}} / T_0 \) within the numerical renormalization group (NRG) approach [5,6] and we shall compare them to predictions from superperturbation theory (SPT) [7].
FIG. 2: $c_T$ vs U/Δ for the symmetric Anderson model calculated within NRG (solid lines with symbols) and SPT (dashed line). Filled circles show $c_T$ using the susceptibility scale $T^0_S$, while filled squares show $c_T$ upon using the scale from the conductance $T^\text{exp}_E$. The relative error in the NRG calculation of $c_T$ lies below 0.2%, considerably more accurate than previous estimates [6]. Inset (a): ratio $T^\text{exp}_E/T^0_S$ vs U/Δ. For U/Δ > 1, the ratio $T^\text{exp}_E/T^0_S$ approaches 1.04.

Fig. 2 shows the dependence of $c_T$ and $c_T^\text{exp}$ on the charging energy $U/\Delta$ with the inset Fig. 2a showing the ratio of Kondo scales $T^\text{exp}_E/T^0_S$ for the symmetric Anderson model together with a comparison of $c_T$ to the SPT result

$$c_T = \frac{\pi^4}{12} \left( 1 + 2R - \frac{1}{2} \right)$$

where $R$ is the Wilson ratio. In the limit of strong correlations, $U/\Delta >> 1$, the Wilson ratio approaches 2 and $c_T$ takes the well known universal Kondo value $c_T = \pi^4/16$ [9,10]. In the opposite limit $U/\Delta >> 0$ the Wilson ratio tends to 1 and $c_T$ acquires the value $\pi^4/12$. Evaluation of Eq. (3) for general $U/\Delta$ requires knowledge of $R$, either from Bethe ansatz or from NRG.

The coefficient $c_R$ is independent of the charging energy $U$ for the particle-hole symmetric case, where it takes the value $\pi^4/16 = 0.617$, which is also recovered exactly within SPT, see Fig. 3. However, experiments use the scale $T^\text{exp}_E$ and measure $c_R^\text{exp}$ as given by Eq. (2). This acquires a $U$-dependence through the $U$-dependence of the ratio $T^\text{exp}_E/T^0_S$ shown in Fig 2 (a). For $U/\Delta = 4.5$, relevant for recent experiments [1], we find from Fig. 3 $c_R^\text{exp} = 0.89$ significantly smaller than the value $c_R^\text{exp} = 5.1$ extracted from the measurements. As discussed in that paper, the large discrepancy between the measured and predicted values of $c_R^\text{exp}$ could indicate the importance of the large spin-orbit interaction present in the InAs quantum dots [1].

In summary, we investigated deviations from the universal Kondo scaling in the linear conductance of a correlated quantum dot due to a finite level asymmetry (i.e., deviation of gate voltage from mid-valley) and a finite local Coulomb repulsion (i.e., finite charging energy) [3]. We determined the behavior of the coefficients $c_T$ and $c_R$ as a function of $U$ and $\Delta$ within NRG and compared these results with SPT [7], finding good agreement for all $U$ at the symmetric point and reasonable agreement for $\Delta = (U - U/2)/\Delta < 0.25$ away from the symmetric point [3].

For the mid-valley conductance, we also determined the ratio of the conductance to susceptibility Kondo scales $T^\text{exp}_E/T^0_S$, allowing us to relate our results for $c_T$ and $c_R$ in terms of $T^0_S$, to the measured coefficients $c_T^\text{exp}$ and $c_R^\text{exp}$ in terms of $T^\text{exp}_E$. While for quantum dots with $U/\Delta > 6$, the difference between the two sets of coefficients is a constant factor of order unity (e.g., $c_T^\text{exp}/c_T^\text{exp} = (T^\text{exp}_E/T^0_S)^2 \approx 1.08$ for $U/\Delta > 6$), for quantum dots with $U/\Delta < 6$ this difference becomes significant and should be carefully taken into account in detailed comparisons of theory with experiment. We expect this to be particularly important for semiconducting quantum dots since $U/\Delta$ is tunable to smaller values in these systems.

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Functional renormalization group study of the Anderson–Holstein model

M. A. Laakso, D. M. Kennes, S. G. Jakobs, and V. Meden
Institut für Theorie der Statistischen Physik, RWTH Aachen

We present a comprehensive study of the spectral and transport properties in the Anderson–Holstein model both in and out of equilibrium using the functional renormalization group (fRG). We show how the previously established machinery of Matsubara and Keldysh fRG can be extended to include the local phonon mode. Based on the analysis of spectral properties in equilibrium we identify different regimes depending on the strength of the electron–phonon interaction and the frequency of the phonon mode. We supplement these considerations with analytical results from the Kondo model. We also calculate the non-linear differential conductance through the Anderson–Holstein quantum dot and find clear signatures of the presence of the phonon mode.

The Anderson–Holstein model, schematically shown in Figure 1, is widely used to describe electronic transport through individual molecules contacted between two leads: The lowest unoccupied molecular orbital is described as a single, spin-degenerate (in the absence of a magnetic field) level of a quantum dot with a Coulomb repulsion between electrons of opposite spin. In addition, the molecule can vibrate at some characteristic frequency $\omega_0$ and the electrons interact with the polarization field generated by this vibration. The coupling of electrons to the vibrational mode is described with a coupling constant $\lambda$, and the dot–lead tunneling rate of the electrons is given by $\Gamma$.

After integrating out exactly both the leads and the phonons we tackle the remaining problem of the interacting electrons on the dot with the functional renormalization group [4]. For the non-equilibrium calculations we use the Keldysh formulation developed for the single-impurity Anderson model (SIAM) in [5]. We use the hybridization to a structureless auxiliary lead, $\lambda$, as the flow parameter and truncate the hierarchy of fRG equations at the second order. This includes all interactions at least to fourth order in $\lambda$ as well as contributions beyond plain perturbation theory by virtue of the RG flow. Since the Keldysh structure of the bare electron–phonon–electron vertex is compatible with the structure used in the flow equations of [5], only the initial conditions of the flow need to be adjusted to account for the phonon-mediated interaction.

For the calculations of equilibrium quantities, e.g., linear conductance, we also use the Matsubara formulation of fRG. To include the local phonon mode we make analogous changes to the initial conditions presented in [6]. In addition, with Matsubara fRG we use a frequency cut-off as the flow parameter to simplify the calculations.

The Anderson–Holstein model has a large number of physical parameters which can be varied, thus making a thorough study of the model complicated. To keep things manageable, we restrict our study to the case of a vanishing magnetic field, and zero temperature. Moreover, to enhance the visibility of phonon-related effects, we will focus on the case where the electron–phonon mediated interaction dominates over the bare Coulomb interaction and therefore set $U=0$. Thus, we are left with the freedom to vary the strength of the electron–phonon coupling, $\lambda/\omega_0$, and the strength of the effective interaction, $2\lambda^2/(\omega_0\Gamma) \equiv U_{ee}/\Gamma$. We will also study how the results change
when the average occupation of the dot is changed by tuning the gate voltage $e V_G$.

The linear conductance as a function of the gate voltage is shown in Figure 2. In general the linear conductance exhibits a peak at a vanishing gate voltage, i.e., at the particle–hole symmetric point. In the case considered here, $U_{\text{spe}} \approx U$, the low-energy excitations are described by charge fluctuations instead of the spin fluctuations of the ordinary SIAM. As a result the roles of the charge and spin are essentially switched. Application of a gate voltage then has a similar effect as the application of a magnetic field in the ordinary SIAM. As a result the width of the peak decreases significantly faster.

![FIG. 2: Linear conductance through the Anderson–Holstein quantum dot as a function of the gate voltage for different values of $U_{\text{spe}}/T$ and $\Delta / \omega_0$. The lines fall roughly into three groups based on the value of $U_{\text{spe}}/T$: Solid lines are obtained with the equilibrium Matsubara formalism and dashed lines with the non-equilibrium Keldysh formalism. Inset shows a comparison to first order perturbation theory (dash-dotted lines).](image)

The width of the peak decreases linearly with increasing $U_{\text{spe}}/T$ and $\Delta / \omega_0$. The lines fall roughly into three groups based on the value of $U_{\text{spe}}/T$: Solid lines are obtained with the equilibrium Matsubara formalism and dashed lines with the non-equilibrium Keldysh formalism. Inset shows a comparison to first order perturbation theory (dash-dotted lines).

![FIG. 3: Differential conductance through the Anderson–Holstein quantum dot as a function of bias voltage for different values of gate voltage and $\lambda / \omega_0 = 1/\sqrt{5} = 0.45$, $U_{\text{spe}}/T = 1.0$, resulting in $\omega_0 / \Gamma = 2.5$, calculated with the Keldysh fRG. Inset shows a comparison to first order perturbation theory (dash-dotted lines).](image)

Additional step close to $e V = 2 \omega_0$, which can be related to the merge and subsequent vanishing of certain features in the spectral density at $\omega = \pm (\omega_0 - eV/2)$ [8]. In first order perturbation theory the kinks at $e V = \omega_0$ are far more pronounced, but the steps at $e V = 2 \omega_0$ are absent. The latter is then clearly a higher order effect.

Majorana fermions coupled to electromagnetic radiation

C. Ohm and F. Hassler
Institute for Quantum Information, RWTH Aachen University, Germany

We consider a voltage-biased Josephson junction between two nanowires hosting Majorana zero modes which occur as topological protected zero-energy excitations at the junction. We show that two Majorana fermions localized at the junction, even though being neutral particles, interact with the electromagnetic field and generate coherent radiation similar to the conventional Josephson radiation. Within a semiclassical analysis of the radiation field, we find that the optical phase gets locked to the superconducting phase difference and that the radiation is emitted at half the Josephson frequency. In order to confirm the coherence of the radiation, we study correlations of the radiation emitted by two spatially-separated junctions [1].

Ever since its discovery, superconductivity has been of great importance for the understanding of quantum coherence. A particular example is the Josephson effect which in the most simple terms can be understood as a dissipationless current which is driven by a gradient of the superconducting phase and thus establishes the macroscopic coherence of the latter. In fact, most of the physical phenomena related to superconducting tunnel junctions are governed by the Josephson equations which have their microscopic origin in a coherent transfer of Cooper pairs through the junction barrier. These equations predict that microwave radiation, also called Josephson radiation, is produced by a voltage-biased tunnel junction [2]. Consequently, the microwave radiation is emitted coherently at the Josephson frequency \( \omega_J = \frac{2eV}{h} \) being proportional to the voltage bias \( V \) across the junction and the transferred Cooper pair charge \( 2e \); here and below, \( e > 0 \) denotes the elementary charge.

Recently, it has been realized that there exists a certain class of superconductors called topological superconductors which are characterized by gapless edge states. Most prominently, it is expected that such a superconductor can be realized by placing a semiconducting nanowire with large spin-orbit interaction on top of a conventional superconductor. As a result mid-gap Andreev states are formed that are localized at the end of the nanowire as well as at the interfaces between two superconductors in a Josephson junction; these edge states are dubbed Majorana fermions and the corresponding Bogoliubov operators are denoted by \( \gamma_j \), see Fig. 1. In contrast to conventional Josephson junctions, also single electrons can be transferred coherently in the presence of Majorana zero modes leading to a \( 4\pi \)-periodic current-phase relationship [3].

In this work, we want to focus on the radiation that arises from coupling Majorana fermions to the electromagnetic field in a voltage-biased Josephson junction which provides coherent radiation at a frequency that is half of the Josephson frequency. Furthermore, there is a mutual relationship between the emitted radiation and the state of the Majorana fermions. As a consequence, the system exhibits correlations between the radiation fields emitted from different sources that are situated far away from each other.

Since we are interested in the Josephson radiation emitted from the single electron transfer, which is due to the presence of Majorana fermions, we imagine the junction to be placed in a microwave cavity supporting a single mode at frequency \( \omega_0 \). The corresponding electrical field operator \( E \) can be written as \( E \approx \frac{\hbar \omega_0}{V} \epsilon (a + a^\dagger) \) with \( \epsilon \) the polarization vector and \( V \) the volume of the cavity. In terms of zero-energy Bogoliubov operators we arrive at the Hamiltonian

\[
H_{dp} = \frac{g}{2} \cos(\phi/2) \gamma_j \gamma_j^\dagger (a + a^\dagger)
\]

FIG. 1: Two bulk s-wave superconductors forming a Josephson junction with superconducting phase difference \( \psi \). On either side there is a semiconducting nanowire which supports Majorana fermions on its ends. We consider the case where the Josephson junction is voltage-biased such that Cooper pairs are emitting radiation at the Josephson frequency \( \omega_J \) while tunneling across the junction (thick wavy line). Due to the presence of the Majorana fermions, also the additional process is allowed which proceeds via tunneling of single unpaired electrons thereby emitting radiation at half the Josephson frequency (thin wavy line). In this paper, we will concentrate on the latter process exclusively.

The applied bias voltage is taken into account by the electromagnetic field \( \mathbf{E} \) and \( \mathbf{B} \) in the presence of Majorana zero modes leading to a \( 4\pi \)-periodic current-phase relationship [3].

The effective light-matter interaction strength

\[
ge \approx \sqrt{\hbar \omega_0 / V} \langle \mathbf{r} \rangle \text{ is the effective light-matter interaction strength.}
\]
the time-dependent superconducting phase difference $\phi(t) = \phi_0 + 2eVt / \hbar$. Here, we assume that is close to the cavity frequency $\omega_c$ and $\omega_c / 2 \gg g$, such that a rotating-wave approximation can be performed. Thus, we end up with a time-independent model Hamiltonian $H_{\text{exp}} = \hbar \Omega a^\dagger a + \hbar \gamma_3 a^\dagger a + \gamma_3 (e^{i \phi_0} a + e^{-i \phi_0} a^\dagger)^3$ with the detuning $\Omega = \omega_c - \omega_f / 2$.

As we are interested in the resonant regime of small $\Omega$, many photons will accumulate inside the cavity due to the driving of the superconducting phase. If the cavity losses are small compared to the pumping rate, the radiation field will approach a classical state with a large photon number $N = \langle a^\dagger a \rangle \gg 1$ and hence $a$ is allowed to be replaced by the complex number $\hat{a}(t) = \langle a(t) \rangle$ in the Heisenberg equation $-i\hbar \frac{d\hat{a}}{dt} = [H_{\text{exp}}, \hat{a}]$. We want to refer to this limit as the semiclassical limit, because $H_{\text{exp}}$ still acts as an operator for the Majorana states depending on the classical field $\hat{a}(t)$. Even though $N$ is expected to become large, we want to demand $\vert g \vert \langle \hat{a} \rangle \ll \Delta$ to avoid interaction with the states above the superconducting gap $\Delta$. The equations of motion for $\hat{a}(t)$ read

$$\dot{\hat{a}} = -i(\Omega + \Gamma) \hat{a} + \frac{g}{2\hbar} \langle \psi(t) \vert \gamma_3 \vert \psi(t) \rangle,$$

where we have introduced the cavity loss rate $\Gamma$ and the (time-dependent) state $\vert \psi(t) \rangle$ of the Majorana fermions.

The initial dynamics of the radiation field is characterized by a highly non-adiabatic time evolution including numerous switches of the electronic system between different eigenstates. However, we are not interested in the transient dynamics and will concentrate on the regime of adiabatic time evolution. In particular, we are interested in the stationary states that turn out to be phase locked to the superconducting phase difference, see below. In the adiabatic regime the matrix elements needed in (2) can be evaluated explicitly. In particular, we find that $\langle \pm \vert \gamma_3 \vert \pm \rangle \equiv T_\phi$ where $\pm$ denotes the two electronic ground states. Plugging the matrix element into the equation of motion (2), it becomes a non-linear differential equation for the field amplitude $\lambda$. We can see that apart from the trivial stationary solution $\lambda = 0$, there is for each eigenstate the second stationary solution

$$\lambda_1 = \pm \frac{g}{4\hbar \sqrt{\Omega^2 + \Gamma^2}} \left( \frac{\text{arctan}(\Omega / \Gamma)}{\gamma_3} \right).$$

The stationary field amplitude depends on the cavity quantities $\Omega, \Gamma$ and the coupling $g$. It can be shown that the nontrivial states are stable (and correspondingly the trivial states unstable).

Regarding the phase of the radiation field (a), we see that it is locked to half of the superconducting phase difference $-\phi_0 / 2$ with an additional phase shift $\text{arctan}(\Gamma / 2\Omega)$ due to the cavity. Moreover, the sign of the radiation field depends on the state of the Majorana fermions. As the broken $U(1)$ phase symmetry of the superconductor is imprinted in the phase of the radiation field the latter is protected from phase diffusion as it is the case for lasers. Therefore, we expect the coherence time of the emitted radiation to be rather long as experiments measuring the relaxation of the persistent current in superconductors have shown that the superconducting coherence lasts for years. As we explain in the next paragraph, these extremely long coherence times cannot be reached in realistic systems due to spontaneous switches of the electronic system called quasiparticle poisoning.

![Diagram](image)

**FIG 2.** Setup to measure the correlation between two spatially separated sources. Each Josephson junction is surrounded by a microwave cavity which emits coherent radiation indicated by beams of radiation $\lambda_s$ and $\lambda_a$. These radiation fields are subsequently used to interfere by a semitransparent mirror (dashed line).

We want to determine the correlation between two different radiation sources $a$ and $b$ for the setup illustrated in Fig. 3. The coherence will show up in the second-order correlation function

$$g^{(2)}_{ab}(\tau) = \frac{\langle \lambda_s(\tau) \lambda_a^\dagger(\tau) \lambda_b(\tau + \tau) \lambda_a(\tau + \tau) \rangle}{\langle \lambda_a^\dagger \rangle \langle \lambda_a \rangle}$$

measuring correlations between two radiation fields $\lambda_a$ and $\lambda_b$. As the phase of the radiation fields is locked to the superconducting phase $\phi_0$ up to the $\pm$ ambiguity depending on the state of the Majorana fermions, dephasing can only happen when the electronic state switches. This happens when quasiparticles are tunneling from a reservoir onto the superconductors. Irrespective of the other details (such as the resistance $R_{\phi}$ of the setup this leads to $g^{(2)}_{ab}(\tau) = e^{-2\phi_0 \tau}$ with the quasiparticle poisoning rate $R_{\phi}$).

In this work, we have analyzed the possibility of coupling Majorana fermions to electromagnetic fields. We have shown that partially coherent Josephson radiation is emitted at half of the Josephson frequency and that its phase gets locked to two possible values. The coherence of the radiation is limited due to rare spontaneous switches of the state of the Majorana fermions which lead to a random flipping of the radiation phase by $\pi$. The interaction of Majorana fermions with radiation could potentially be utilized for addressing and manipulating the quantum information encoded in the Majorana states.

CuNCN, mysterious quantum spin-liquid

A. L. Tchougréeff and R. Dronskowski
Institute of Inorganic Chemistry, RWTH Aachen University, Germany

CuNCN, a novel copper carbodiimide, exhibits contradictory physical properties, namely a Cu(II)–N coordination conforming to a 1st order Jahn–Teller effect, the total absence of magnetic neutron scattering, and a fairly complex temperature dependence of its magnetic susceptibility including Pauli- and Arrhenius-like regimes. A many-body spin-liquid (resonating valence bond, RVB) state of the antiferromagnetically interacting but frustrated spins in CuNCN allows for a vivid physicochemical picture and predicts three RVB states differing in their dimensionalities at different temperatures. The RVB theory semiquantitatively describes subtle (and even paradoxical) structural effects in the lattice parameters within the entire temperature range.

Within the last decade, we have predicted, synthesized and characterized the antiferromagnetic 3d carbodiimides incorporating divalent 3d cations connected by the NCN$^{2-}$ carbodiimide dianions [1], hence chemical relatives of the correlated oxides. All MNCN compounds with $M = Mn$–Ni represent a uniform family of optically transparent antiferromagnetic insulators but the compound CuNCN [2] falls out of the row. Although its structure (Figure 1) can be understood to originate from a 1st order Jahn–Teller distortion of the archetypical MNCN structure, other properties are quite bizarre. First, CuNCN is a deeply black but nonmetallic material. Second, its magnetic moments do not manifest themselves in spin-polarized neutron scattering [2]. Third, the susceptibility as a function of temperature is complex with at least two distinct regimes: a temperature-independent (Pauli-like) paramagnet above 80–100 K which switches to a gapped (Arrhenius-like) one below. These contradictory observations must be reconciled, in particular touching upon (i) the absence of the magnetic scattering and (ii) two regimes of the temperature course of the susceptibility. We mastered this theoretical challenge by assuming quantum spin-liquid (or resonating valence bond, RVB) phases of electronic spins to occur in CuNCN [3]. Although the RVB states have been known in theoretical chemistry for more than a century (see the well-known RVB approximation for benzene in Figure 2), none of existing solid-state quantum chemistry packages implements them.

First, we extended the RVB treatment of the finite system exemplified by benzene to infinite CuNCN by assuming the antiferromagnetic interactions for the unpaired electrons (spins) residing in the $d^9$-shells of Cu$^{2+}$.

FIG. 1: The crystal structure of CuNCN and the exchange parameters. The magnetic model of the ac plane includes the $J_c$, $J_a$, and $J_{ac}$ interactions. Magnetic frustration appears when the interactions shown in red and black are simultaneously present. Reprinted with permission of IOP from [3].

The corresponding exchange interactions $J_c$, $J_a$, and $J_{ac}$ are shown in Figure 1 and run in the crystallographic ac plane.

In the RVB state one does not expect any magnetic neutron scattering since the type of order in it differs from the one detectable by a neutron experiment because the spins form all possible pairings as shown in Figure 3. Another feature characteristic of the RVB states in the infinite systems is a rather peculiar spectrum of the quasiparticles: spinons. These are of the fermion statistics, just like electrons: they bear spin $\frac{1}{2}$, but no charge.

FIG. 2: Pictorial representation of the RVB state of the benzene molecule. Two Kekulé structures and the three Dewar structures contribute, and a single parameter ($\psi$) suffices to completely describe the depicted RVB function due to symmetry reasons. Double sticks symbolize that the spins located on the corresponding atoms are coupled (paired) into the “valence bond state”.

For our CuNCN model the excitation spectrum and related physical properties are different in the different temperature ranges, as shown in Figure 4. The spinon spectrum shows different regimes, too, and a rich variety of magnetic behaviors depending on the order parameters $A$, $B$, and $C$. If $C$, but not $A$, is nonvanishing, the spectrum is gapless for spinons propagating in the dispersion law and the density of $c$ direction.
corresponding quasiparticle densities of states (qDoS) are shown in Figure 4 (upper row); \( C \) refers to the saddle points and marks the position of the logarithmic peak in the qDoS.

![Figure 3: Pictorial representation of the characteristic spin-pairings (valence bonds) contributing to various RVB states involved in the explanation of the CuNCN physics; adapted with permission of IOP from [3].](image)

This state is quasi-one-dimensional, hence dubbed Q1D; the pairings extending only in the c direction are depicted in the left column of Figure 3, and the qDoS is finite at zero energy. This produces the Pauli magnetic susceptibility observed above 100 K.

![Figure 4: Characteristics of three RVB phases of CuNCN involved in the explanation of the temperature course of the magnetic susceptibility.](image)

If \( A, C \neq 0 \), the spinon dispersion law has no nodal lines, but four nodal points with vanishing spinon energies. The dispersion laws then feature saddle points, the pseudogaps \( A \) and \( C \). These states are two-dimensional, hence 2D, where the pairings extend in the a and c directions as depicted in the middle and right columns of Figure 3. The qDoS develop two logarithmic singularities at \( A \) and \( C \), as shown in the middle and bottom of Figure 4. Likewise, the lower of the two pseudogaps guarantees the Arrenius law for the susceptibility and takes the part of the activation energy in it.

The hypothesis of the Q1D and 2D spin-liquid states of CuNCN explains two key facts of its physics: two temperature regimes of the susceptibility and the absence of the magnetic scattering. However, there are other possibilities: the spin-Peierls scenario [4] would explain this behavior equally well since its spectrum is also gapped and all spins are paired. Different to RVB, in the spin-Peierls states the pairings appear regularly, that is, alternating: each odd or even pair of spins are paired, producing a variety of spin-Peierls phases. Regular distributions of pairings in spin-Peierls states must exhibit structure manifestations through the relevant alternation of the interatomic separations [4]. This immediately asks for structural methods to distinguish between the spin-liquid and spin-Peierls options.

Structural studies (synchrotron [5] and neutron [6]) consistently indicate a typical shrinking of the CuNCN crystal upon temperature lowering. No trace of alternation of interatomic separations crucial for the spin-Peierls scenario is detected. Contrarily, the sense of the temperature course for the lattice parameter \( a \) distinctly changes: its decrease switches to an increase, right at the point where the temperature regime of the magnetic susceptibility switches from Pauli to Arrhenius type. Remarkably, an extra decrease of the lattice parameter \( c \) accompanies this, as theoretically predicted for the transition from Q1D to 2D. Indeed, the observed increase in \( a \) requires an extra decrease of \( c \), just as observed.

Even more intriguing events evolve at lower temperatures (30 K) when the \( c \) parameter changes the sign of its temperature slope. This is attributed to a transition between two 2D RVB phases in the ac planes of CuNCN. The 2D RVB phases with \( A, C \neq 0 \) exist in two versions [3], with \( B \neq 0 \) and with \( B = 0 \), shown in the middle and right columns of Figure 3, respectively, while the spinon spectra are found in the middle and bottom of Figure 4. The 2D RVB phase with \( A, B, C \neq 0 \) installs at 100 K by opening the pseudogap \( A \) for the spinons propagating in the a direction [6]. The lowest-energy 2D RVB phase is, however, that with \( A, C \neq 0 \), and \( B = 0 \) installing at 30 K and persisting down to zero temperature. It features a temperature dependence of the pseudogap \( C \) which manifests in that of \( c \) changing the sign of its slope vs. temperature.

Summarizing, a consistent description of the mysterious CuNCN physics is possible by using new spin-liquid RVB states of its spins in the ac plane.

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Magnons play an important role in fast precessional magnetization reversal processes serving as a heat bath for dissipation of the Zeeman energy and thus being responsible for the relaxation of magnetization. Employing ab initio many-body perturbation theory we studied the magnon spectra of the tetragonal FeCo compounds considering three different experimental c/a ratios, c/a = 1.13, 1.18, and 1.24 corresponding to FeCo grown on Pd, Ir, and Rh, respectively. We find that for all three cases the short-wave-length magnons are strongly damped and tetragonal distortion gives rise to a significant magnon softening. The magnon stiffness constant $D$ decreases almost by a factor of two from FeCo/Pd to FeCo/Rh. The combination of soft magnons together with the giant magnetic anisotropy (GMA) energy suggests FeCo/Rh to be a promising material for perpendicular magnetic recording applications.

Since the introduction of the first commercial hard disk drive in 1956, the recording density in a hard disk, that is the amount of information that can be stored per square inch, has increased by more than 7 orders of magnitude to meet an ever-growing need. This has been achieved by a simple scaling of the dimensions of the bits recorded in storage medium. Due to the superparamagnetic effect, however, the recording density has an upper limit. For longitudinal magnetic recording it is around 200 gigabit per square inch, whereas it is predicted to be much larger for perpendicular recording, up to 1000 gigabit per square inch, though this limit is constantly changing with the discovery of new materials [1].

The major problem in designing magnetic storage media is to retain the magnetization of the medium over a long period of time despite thermal fluctuations. If the ratio of the thermal energy $k_B T$ to the magnetic energy per grain $K_m V$, where $V$ is the grain volume and $K_m$ is the uniaxial magnetic-crystalline anisotropy energy (MAE), becomes sufficiently large, the thermal fluctuations can reverse the magnetization in a region of the medium destroying the data stored there [1]. In order to further increase the recording density in future recording media, high-$K_m$ materials are needed. Additionally, a large saturation magnetization $M_s$ is beneficial to reduce the write field, which has to be applied by the write head. Materials that combine the desired large values of $K_m$ and $M_s$ are tetragonal near-equiaatomic FeCo alloys. The large values of $K_m$ and $M_s$ in these alloys were first predicted by first-principles calculations [2] and then confirmed by experiments [3]. In particular, Yildiz et al. [3] achieved a strong perpendicular magnetic anisotropy (PMA) in tetragonal FeCo alloys epitaxially grown on Pd ($c/a = 1.13$), Ir ($c/a = 1.18$), and Rh ($c/a = 1.24$) substrates. The authors found that the PMA is very sensitive to the tetragonal distortion and increases with increasing c/a ratio, which allows to tune the PMA by growing the alloys on different substrates.

Besides large $K_m$ and $M_s$ values, another very important issue in magnetic recording applications is the magnetic switching time, which imposes physical limits on data rates and areal recording densities [4]. In current devices the switching speeds have reached a point where dynamical effects are becoming very important. Magnons are created in fast (field driven) as well as ultrafast (laser induced) magnetization reversal processes. The former case is of particular interest for current device applications. It is found that above some threshold magnetic field the uniform precessional mode, i.e., the $k = 0$ magnons decay into nonuniform magnons ($k \neq 0$), i.e., the Zeeman energy stays in the magnetic subsystem and scatters between magnon modes [5]. The Landau-Lifshitz-Gilbert (LLG) equation with a phenomenological damping constant $\alpha$ is commonly employed to describe magnetization dynamics of small-angle precessional switching. However, recent studies have shown that in the case of large-angle (fast) switching, in which the magnons are created, the LLG equation should be extended in several aspects [6], in particular a $k$-dependent damping constant $\alpha_k$ has been proposed [6], which allows short-wave-length magnons to relax faster than those with $k \to 0$. Thus, the magnetization relaxation processes, specifically the damping of magnons, play an important role in designing ultrahigh-density magnetic recording media.

Using a recently developed Green-function method based on the many-body perturbation theory in the $GW$ approximation in combination with the multiple-scattering $T$ matrix in a Wannier basis [7], we have calculated the dynamical spin susceptibility (DSS) of tetragonal FeCo compounds whose $c/a$ ratios were fixed to the experimentally determined values that relate to the three different substrates [3, 8]. Within many-body perturbation theory the transverse DSS, $\chi^{+\perp}$, can
be schematically written as $\chi^{t+} = \chi_{KS}^{t+} + \chi_{KS}^{t+} T^{-} + \chi_{KS}^{t+} T^{-}$, where the first term on the right-hand side represents the response of the noninteracting system, i.e., the Kohm-Sham DSS. The second term contains the $T$ matrix, which is given by $T^{-} = \left[1 - W \chi_{KS}^{-}\right]^{-1} W$, where $W$ is the screened Coulomb interaction. The $T$ matrix describes dynamical correlation in the form of repeated scattering events of particle-hole pairs with opposite spins and is responsible for the formation of collective magnon excitations. The DSS provides complete information on the magnetic excitation spectrum including collective magnon modes as well as single-particle Stoner excitations together with their respective lifetimes.

As the unit cell of the FeCo compounds contains two magnetic atoms, the calculated magnon dispersions exhibit two branches as shown in Fig. 1: an acoustic and an optical branch. The former persists throughout the Brillouin zone indicating a localized nature of magnetism in FeCo compounds. The optical branch, on the other hand, is heavily damped due to the coupling to single-particle Stoner excitations.

We find that the tetragonal distortion gives rise to significant magnon softening. The average magnon stiffness constant $D$ decreases almost by a factor of two from FeCo/Pd ($D_{\text{avg}} = 560$ meVÅ²) to FeCo/Rh ($D_{\text{avg}} = 289$ meVÅ²), which means that acoustic magnons can be excited much more easily in the latter material than in the former one. In field-driven fast magnetic switching processes, which take place on a time scale of ns to 100 ps, the excess Zeeman energy will be transferred to the acoustic magnons. Thus, the magnon stiffness constant $D$ and the life time of $k \neq 0$ magnons play a decisive role in determining the strength of the switching field and switching time. The latter is limited by the damping of magnons. Furthermore, the damping also prevents the "back-switching" effect, which reduces the data rates in magnetic recording devices.

In summary, we have calculated the magnon spectra of the tetragonal bulk FeCo compounds from first principles considering three different experimental $c/a$ ratios: FeCo grown on Pd, Ir, and Rh with $c/a$ =1.13, 1.18, and 1.24, respectively. We have found that for all three cases the short-wave-length magnons are strongly damped and tetragonal distortion gives rise to a significant magnon softening. The magnon stiffness constant $D$ decreases almost by a factor of two from FeCo/Pd to FeCo/Rh, which reduces the switching field and yields efficient excitation of the $k \neq 0$ magnons. Furthermore, the obtained strong damping of large-wave-vector magnons in FeCo compounds suggests a $k$-dependent damping constant $\alpha_k$ in the LLG equation in describing magnetization dynamics of large-angle fast precessional switching. Combination of soft magnons with their substantial damping at large wave vectors as well as giant MAE suggests FeCo/Rh to be a very promising material for ultrahigh-density perpendicular magnetic recording applications.

Berry phase effects in chiral magnets from first principles theory

F. Freimuth, S. Blügel, and Y. Mokrousov
Peter Grünberg Institut-1 and Institut for Advanced Simulation-1, Forschungszentrum Jülich, Germany

It has been known for quite some time that the non-trivial spatial distribution of the magnetization in chiral magnets can give rise to the Berry phase effects for electrons, which propagate through such a texture. One of the most prominent manifestations of such Berry phases is the so-called topological Hall effect, the existence of which was speculated phenomenologically and was hinted at by recent magneto-transport experiments. Here we report on the first microscopic justification of the existence of the topological Hall effect from material-specific first principles theory. We also point out that, while the topological and anomalous Hall effects are the manifestations of two limiting Berry phases, the presence of spin-orbit coupling in chiral magnets manifests in an additional Berry phase contribution which gives rise to the Dzyaloshinskii-Moriya interaction and an electrical charging of skyrmions.

In the past 15 years a general understanding has emerged that the anomalous Hall effect (AHE) in collinear ferromagnets often comes from the Berry phases which Bloch electrons pick up as they travel in reciprocal space. The final trust in the role of the \( k \)-space Berry phase contribution to the AHE has been granted by numerous first principles calculations of the Berry phase AHE in various materials of different complexity often performed \textit{en par} with experiments on the same compounds. The first work of this kind dates back to the year of 2004.

Since then it was also independently speculated that the spin of an electron which travels in space through a spin texture of spatially varying magnetization will pick up the Berry phase in very much the same way as electrons do in reciprocal space of a collinear ferromagnet. Due to specific structure of the Hamiltonian which describes the coupling of the electron spin to the texture, such a Berry phase can be seen as a phase an electron wavefunction picks up as it travels in a collinear magnet subject to an external magnetic field. This magnetic field is called an emergent magnetic field \( B_e \) and it is proportional to the rate with which the magnetization changes in space. This in turn suggests that the propagating electron will be subject to a Lorentz force thus giving rise to the Hall effect. What distinguishes this Hall effect from the well-known ordinary Hall effect (OHE) is that the sign of the emergent magnetic field is opposite for electrons of opposite spin. The corresponding transverse phenomenon is called the topological Hall effect (THE), so as to emphasize its origin in the non-trivial topology of the spin texture in real space.

![FIG. 1: Comparison between experimental (on the left) and theoretical (on the right) values for the anomalous and the topological Hall signal as a function of ordered moment in the zero-temperature limit in Mn\(_{1-x}\)Fe\(_x\)Si alloys. The values presented are for the anomalous Hall conductivity (upper panel) and topological Hall constant (lower panel), taken from [1]. Note, that the value of the ordered moment decreases with increasing Fe concentration.](image-url)

Up to now, the THE was speculated to exist in a family of B\(_{20}\) compounds. This speculation is based on Hall measurements which show an additional contribution to the Hall effect as the applied magnetic field is varied and the system goes through a skyrmion spin texture phase in its magnetic phase diagram. The most studied benchmark material in this respect is MnSi. However, it is known that MnSi has a very complicated electronic structure with very non-trivial magnetic properties and complex multi-sheeted \( d \)-electron Fermi surface. So far, this obstacle made it impossible to claim that the additional Hall signal measured in the skyrmion phase of MnSi comes undoubtedly from the real-space texture driven Berry phases. Formulating such a clear statement has been the goal of our recent theoretical and experimental study [1].

For this purpose, we considered the family of MnSi-based alloys: Mn\(_{1-x}\)Fe\(_x\)Si. The properties of these alloys, such as their magnetization, phase diagram and, importantly, Hall transport properties, were measured experimentally as a function of the Fe concentration \( x \). From the measurements of the ordinary Hall and anomalous Hall constants in varying external magnetic field the values of the topological Hall constant in the skyrmionic phase of the alloys were also determined as a function of \( x \). Interestingly, it was observed that while for small \( x \) the AHE and THE change sign, for larger doping
AHE remains small and the THE grows in magnitude by over a factor of 10, see Fig. 1.

Recently, we realized that although the real-space and reciprocal space Berry phases, which respectively give rise to the THE and AHE, are the two limiting cases, there can be a contribution to the Berry phase which comes from coupling between the real-space and reciprocal space coordinates [2]. Such coupling in chiral magnetic structures is realized via the spin-orbit interaction, which couples the direction of the magnetization in real space to the electronic structure of the system in reciprocal space. Clearly, the so-called mixed Berry phase influences the transverse transport properties and leads to a non-trivial coupling between the AHE and the THE.

However, the effect of the real-space–reciprocal-space coupling can be seen already at the level of the energetics of the system. To demonstrate this we derived the expression for the redistribution of the free energy in a ferromagnetic system due to spin chirality, and showed that it can be expressed in terms of the mixed Berry phase [2]. An example of such redistribution computed from first principles is shown for the case of MnSi in Fig.2. By noticing that the chirality-driven energy correction is naturally related to the celebrated Dzyaloshinskii-Moriya interaction (DMI), we derived the mixed Berry phase expression for the DMI, which is conceptually analogous to that for the orbital magnetization in terms of the reciprocal Berry phases [2, 3].

Another manifestation of the mixed Berry phase changes in the energetics is the chirality-driven charging of skyrmions [2]. Finally, we remark that the mixed Berry phase is intrinsically related to the phenomenon of the spin-orbit torque, inserted by an electrical current on the magnetization of collinear ferromagnets [3,4].

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Mathematical analysis of chiral skyrmions

Christof Melcher
Lehrstuhl I für Mathematik, RWTH Aachen University, Germany

Chiral skyrmions are topologically non-trivial spin configurations emerging in magnets without inversion symmetry. Recent theoretical and experimental advances, which in particular led to the observation of skyrmionic structures down to the atomic scale (see e.g. [1,2]), and the strikingly simple mathematical model on the other hand, also call for a rigorous approach based on variational methods. In recent work we established a parameter regime where isolated skyrmions emerge as relative minimizers in a non-trivial homotopy class.

The description of a magnetization distribution in terms of a continuous vector field \( m : \Omega \rightarrow S^2 \) from a domain \( \Omega \subset \mathbb{R}^3 \), representing the magnetic sample, into the unit sphere \( S^2 = \{ y \in \mathbb{R}^3 : |y| = 1 \} \), i.e. the space of directions, offers the possibility to introduce concepts from topology, i.e., the classification of local magnetization patterns according to their homotopy type. One may say that a magnetization configuration is topologically non-trivial if it cannot be deformed continuously into a uniform state. However, this classical concept, originally introduced in the framework of boundaryless manifolds, has the disadvantage of requiring appropriate boundary conditions. An alternative approach is to classify (local or global) structures according to their topological index. The relevant indices in magnetism are the Brouwer degree and the Hopf index, which reflect the topology of 2D and 3D spin structures, respectively. The advantage is that these indices admit integral representations with topological charge densities

\[
\omega_{3D}(m) = m \cdot \partial_i \xi, \quad \text{and} \quad \omega_{3D}(m) = F \cdot A
\]

satisfying \( \nabla \cdot F = 0 \) and with vector potential \( A \). The topological type can be related to the governing energy functionals, which is the starting point of mathematical analysis. This happens in particular through \( \text{ansatz-free} \) topological lower bounds, which can often be used to identify topologically non-trivial structures as stable or metastable states. The notion of topological protection can then be explained energetically in terms of energy barriers that have to be overcome in order to change the global structure.

A well-known example of a topologically non-trivial 2D structure emerging in soft magnetic films is a magnetic vortex, i.e., the section of a Bloch line with the cross section of the film plane. The stabilization of magnetic vortices is mainly due to the interplay of exchange and dipolar interaction. The pole avoidance principle (i.e. minimality of dipolar energy) drives the formation of (almost solenoidal) flux closure patterns of non-trivial topology. A mathematical idealization is to enforce such patterns through a curling boundary condition in order to fully avoid magnetic surface charge. Considered as a map, the vortex covers only a hemisphere. Accordingly, the topological charge of a vortex is a half-integer \( q = \pm 1/2 \) (depending on the orientation) and is concentrated in the vicinity of the vortex core [3]. Another example emerging in magnetic films with strong uniaxial anisotropy perpendicular to the film plane are magnetic bubbles. Those are domains of up or downward magnetization, which are surrounded by a 180-degree domain wall, along which the topological charge concentrates. The topological index of the global object, which covers the entire sphere, is \( q = \pm 1 \), depending on the orientation.

Magnetic chiral skyrmions emerge in the presence of Dzyaloshinskii-Moriya interaction (DM), which originates from reduced geometric or crystalline symmetry in combination with spin-orbit coupling. A rather general mathematical description of chiral interactions is based on the components of the vector-valued differential one-form

\[
\Lambda(m) = m \times \partial_i, \quad dx^a,
\]

referred to as Lifshitz invariants. Chiral skyrmions have topological charge \( q = \pm 1 \), which, in contrast to magnetic bubbles, is localized near the center. Profiles are sharply localized with exponential tails. Depending on the specific parameter regime, chiral skyrmions appear as single localized topological solitons, or they arrange in a regular lattice. Variational models which accommodate chiral skyrmions as metastable states are surprisingly simple. For direction fields \( m : \mathbb{R}^2 \rightarrow S^2 \) from the plane \( \mathbb{R}^2 \) to the unit sphere \( S^2 \), a showcase energy functional

\[
E(m) = \int_{\mathbb{R}^2} \epsilon(m) \, dx
\]

has a density which combines Heisenberg exchange, DM, and Zeeman interaction

\[
\epsilon(m) = \frac{1}{2} | \nabla m |^2 + \kappa \, m \cdot (\nabla \times m) + \frac{h}{2} | m - \hat{e}_3 |^2
\]

with coupling constants \( \kappa \neq 0 \) and \( h > 0 \), both normalized by the exchange constant. For simplicity and in order to highlight the chiral effect we disregard contributions from crystal and shape anisotropy. By virtue of the co-area formula, the DM term can be rewritten as
\[ \kappa \int_\mathbb{R}^3 m \cdot (\nabla \times m) \, dx = 2\kappa \int_0^1 \int_{\partial Q(t)} m \cdot dx \, dt, \]

which shows that effect of DM is maximal if the horizontal magnetization \( m = (m_1, m_2) \) is tangential to level curves of \( m_3 \). The topological constraint is formulated by means of the topological charge

\[ Q(m) = \frac{1}{4\pi} \int_{\mathbb{R}^3} m \cdot \partial_1 m \times \partial_2 m \, dx, \]

i.e. the Brouwer degree \( q = \text{deg}(m) \). In-plane curling preferred by DM interaction and the asymptotic state \( m(x) \rightarrow \hat{e}_3 \) as \( |x| \rightarrow \infty \) selected by Zeeman interaction suggest \( Q(m) = -1 \) (for the reverse field we expect \( Q(m) = +1 \)). The stabilization of topological solitons due to DM interaction differs significantly from the classical Skyrme mechanism. Recall the density of the 2D Skyrme energy functional, see e.g. [4]

\[ \epsilon_{\text{skyrme}}(m) = \frac{1}{2} \left| \nabla m \right|^2 + \kappa \left| \partial_1 m \times \partial_2 m \right|^2 + \frac{\hbar}{2} \left| m - \hat{e}_3 \right|^2. \]

The main effect of the Skyrme term (middle term) is a higher integrability of the topological charge density, which prevents the system from collapsing [5]. In contrast, the stabilization of chiral skyrmions is not due to a regularizing effect; it is based on the fact that chiral modulations can lower the minimal energy below a point, where a blow-up scenario is energetically preferred. Our reasoning led to the following existence result.

**Theorem** Suppose \( \kappa \neq 0 \) and \( h \geq 2\kappa^2 \). Then the minimum of \( E(m) \) among all admissible fields with \( Q(m) = -1 \) is attained by a smooth field \( m \) in this homotopy class. The least energy in all other non-trivial homotopy classes is strictly larger.

**The mathematical argument.** Our method of proof is based on direct minimization by means of a sequence of configurations \( (m_n)_{n \in \mathbb{N}} \) with \( Q(m_n) = -1 \) and \( E(m_n) \rightarrow \min \). The main difficulty is that for generic sequences of configurations the topological charge may concentrate or part of it may escape to infinity, such that the topological constraint is not preserved in the weak limit. In order to rule out these scenarios, we exploit the minimization property of \( (m_n)_{n \in \mathbb{N}} \). For this purpose we consider, for arbitrary integers \( q \), the least upper bound for the energy in the class of fields with topological charge \( q \)

\[ I_q = \inf \{ E(m) | Q(m) = q \}. \]

A keystone in the proof of our existence result we show the following topological energy estimate is valid for \( h \geq 2\kappa^2 \):

\[ I_q \leq I_4 < 4\pi \leq I_q \quad \text{for all} \quad q \not\in \{0, -1\}. \]

First of all, for arbitrary \( \kappa \neq 0 \) and \( h \geq 0 \), a trial field \( m \) can be constructed with \( Q(m) = -1 \) and such that \( E(m) < 4\pi \). For \( h \geq 2\kappa^2 \) we obtain a lower bound \( E(m) \geq 2\pi q \) for all \( m \) with \( Q(m) = q \). Hence it remains to prove \( E(m) \geq 4\pi \) if \( Q(m) = 1 \).

In order to exploit the algebraic structure of DM interaction, we introducing helical derivatives

\[ D_n m = \partial_n m - \kappa (\hat{e}_3 \times m). \]

The name is motivated by the fact that \( D_n m = 0 \) for helical fields \( m \), performing a rotation of constant frequency \( \kappa \) perpendicular to the \( \hat{e}_3 \) axis, i.e., the ground state in the absence of an applied field. In this framework exchange and DM interaction can be combined in one term

\[ \frac{1}{2} \left| \nabla m \right|^2 + \kappa m \cdot (\nabla \times m) = -\kappa^2 + \frac{1}{2} \sum_{\alpha=1}^3 |D_{\alpha} m|^2. \]

The argument can be refined leading to a topological lower bound for fields \( m \) with positive skyrmion number \( Q(m) = q \)

\[ \int_\mathbb{R}^3 \left( \frac{1}{2} \left| \nabla m \right|^2 + \kappa m \cdot (\nabla \times m) \right) dx \]

\[ \geq 4\pi q - \frac{\kappa^2}{2} \int_\mathbb{R}^3 \left| m - \hat{e}_3 \right|^2 dx. \]

We obtain in particular \( E(m) \geq 4\pi \) if \( Q(m) = 1 \) and \( h \geq \kappa^2 \). The topological energy bounds enable us to carry out the proof of existence by virtue of the so-called concentration-compactness principle, see [6]. Our analysis suggests that higher index configuration (i.e. multiple skyrmions) will emerge as metastable states at lower fields. An important step towards a rigorous analysis of the complete phase diagram is to provide more refined topological upper and lower bounds for least energies for a broad range of \( h \) an \( \kappa \). An outstanding mathematical question is to identify the hexagonal lattice as optimal arrangement for a multi skyrmion configuration. Striking progress has been made towards the rigorous explanation of Abrikosov lattices of Ginzburg-Landau vortices in superconductivity, whose energetic optimality can be related to deep results from number theory [7].

Spintronic magnetic anisotropy

M. Misiorny¹, M. Hell¹, and M. R. Wegewijs¹,²

¹ Peter Grünberg Institut-², Forschungszentrum Jülich, Germany
² Institute for Theory of Statistical Physics, RWTH Aachen University, Germany

We predict that superparamagnetism – the preferred alignment of a spin along an easy axis – may arise in a broad class of quantum-dot systems with spin $S > 1/2$ without spin-orbit interaction: simply by contact with ferromagnets a spintronic exchange field of quadrupolar nature is generated locally. This is equivalent to a magnetic anisotropy barrier opposing reversal of the spin and can be observed in conductance measurements. Analogously to the spintronic dipolar exchange field, responsible for the well-known spin torque, the effect is susceptible to electric control and increases with tunnel coupling as well as with spin polarization.

The growing interest in nanomagnets such as magnetic adatoms and single-molecule magnets is fueled by prospects of their application in novel spintronic devices whose functionality derives from their unique magnetic features. One of their key properties is a strong magnetic anisotropy leading to magnetic bistability, required for building blocks for nanoscale memory cells and non-trivial quantum dynamics, useful for quantum information processing. In either case, operational stability of such devices hinges heavily on the height of the energy barrier opposing the spin reversal. Though recently progress has been made in the control over the magnetic anisotropy by various means, achieving a high spin-reversal barrier still remains a challenge. By incorporating a nanomagnet into an electronic circuit its magnetic properties may be significantly altered, which can be advantageous. For instance, a spintronic route for manipulation of nanomagnets entails ferromagnetic electrodes and uses the spin torque due to spin-polarized scattering or Coulomb interaction, a magnetic proximity effect. Here we present a new route, combining spintronics with molecular magnetism [1]: high-spin quantum dots can acquire a significant magnetic anisotropy that is purely of spintronic origin, instead of deriving from spin-orbit interaction. Besides providing an alternative approach to electrical manipulation and engineering of superparamagnetic nanomagnets, this new spintronic quantity, the quadrupolar exchange field, is found to be of key importance for the analysis of experiments that probe atoms or molecules using highly spin-polarized electrodes.

The origin of superparamagnetism, usually dominating the magnetic behaviour of a nanomagnet, is a magnetic anisotropy energy barrier. For instance, an adatom with a spin-degenerate ground multiplet (quenched orbital moment), is described by the generic spin Hamiltonian

$$H_{eff} = B\hat{S}_z + D\hat{Q}_{zz},$$

where $\hat{S}_z$ denotes the $z$-component of the total spin, here $S = 1$, and $\hat{Q}_{zz} = \hat{S}_z^2 - S(S + 1)/3$ is a spin-quadrupole moment. Here $B$ is an external (dipolar) magnetic field. The spin-orbit interaction induces an intrinsic anisotropy, a quadrupolar field $D$ which is often of the easy-axis type ($D < 0$): the spin is aligned with the $z$-axis but without favouring a particular orientation along it. The corresponding energy splitting is sketched in Fig. 1A. By probing their ligand environment, the atomic electrons thus experience a broken spin symmetry.
In spintronics, a very similar situation, depicted in Fig. 1B, arises in a completely different physical setting where spin-orbit interaction is negligible. Electrons localized in spin-isotropic quantum dot with a high-spin (S > 1/2) probe the broken spin symmetry in attached ferromagnets by virtual charge fluctuations, resulting in a spin current and a spin-torque. The latter can be described by replacing the externally applied magnetic field \( B \) in Eq. (1) by an effective exchange field \( \propto \Gamma \). For low spin S = 1/2 this is well understood: the exchange field depends on the gate voltage \( \varepsilon \) (= level position) in an antisymmetric way, \( B(\varepsilon) = -B(-\varepsilon - U) \), reversing its sign at the symmetry point \( \varepsilon = -U/2 \), deep in the Coulomb blockade, as experimentally observed [2]. Approaching the symmetry point, processes of higher order in the tunneling rate \( \Gamma \) become increasingly important, which are responsible for inelastic tunneling, as well as the Kondo effect, both primary experimental tools in atomic-scale spin detection and manipulation [3]. For high-spin quantum dots, e.g. an S = 1 quantum dot with triplet ground state as sketched in Fig. 1C, this results in a drastically different situation. An additional easy-axis spintronic anisotropy term of the same form as the second term of Eq. (1) appears which is absent for low spin S = 1/2. In the limit of deep Coulomb blockade \( |\varepsilon + U/2| \ll U/2 \) we obtain an all-spintronic superparamagnet described by Eq. (1) with a constant anisotropy \( D^* \) and a magnetic field that is linearly tunable by the gate voltage through \( \varepsilon \): for singlet excitation and large band width \( W \gg U \gg T \gg \Gamma \)

\[
B(\varepsilon) \approx -\frac{2}{\pi} p \Gamma \frac{\varepsilon + U/2}{U} \tag{2}
\]

\[
D(\varepsilon) \approx \frac{1}{\pi} (p \Gamma)^2 \frac{2W}{U} \ln \frac{U}{\varepsilon} \approx D^* \tag{3}
\]

This is entirely analogous to the uniaxial spin anisotropy typical to magnetic atomics or molecules, cf. Fig. 1A. However, this anisotropy is induced by the proximity of the ferromagnet and displays the characteristic properties of a spintronic exchange field: it is electrically tunable by the gate voltage and scales as \( \propto p^2 \Gamma^2 \). It is thus enhanced with increasing tunnel coupling \( \Gamma \), similar to the Kondo effect (see below), but in contrast, it is also enhanced with increasing spin polarization \( p \), which suppresses the Kondo effect. By attaching the ferromagnets we have thus obtained an artificial molecular magnet, whose quadrupolar field \( D \) is strong enough to suppress the Kondo effect in a wide range of parameters. The above perturbative results (2)-(3) are confirmed to give a clear transport signature for strong tunnel coupling \( \Gamma \) by DM-NRG calculations shown in Fig. 2: Instead of the peak in Fig. 2a for \( S = 1/2 \), we find in Fig. 2b for \( S = 1 \) a pronounced gap. At the symmetry point (where \( B = 0 \)) there is still a definite spin excitation which can only be due to nonzero \( D \).

This has important experimental implications: not only does spintronic anisotropy modify an existing, intrinsic anisotropy barrier (induced by spin-orbit interaction), but it can also create such a barrier from scratch (without spin-orbit coupling): the excitation spectrum can thus be generated merely by interaction with a magnetic tunnel probe. Conservative estimates show that the spintronic anisotropy barrier can be as large as for state-of-the-art real single-molecule magnets. High-spin quantum dot spin valves thus exhibit a novel tunable interplay of spintronics and nanomagnetism that is not possible for low-spin quantum dots. It allows for fast, all-electric spin operations, which are challenging for atatoms and single-molecule magnets, and on-demand magnetic bistability. Finally, in contrast to intrinsic anisotropy, the spintronic anisotropy can also be turned off magnetically by simply switching the spin valve to the antiparallel configuration.

Spin waves in thin films

R. Jayaraman, E. Michel, H. Ibach, and C. M. Schneider
Peter Grünberg Institut-6, Forschungszentrum Jülich, Germany

Using a recently developed advanced electron energy loss spectrometer we have studied high energy/high momentum spin waves in ultrathin ferromagnetic films. We have shown that the finite penetration depth of electrons enables the observation of spin waves localized at metal/metal interfaces. Due to the high energy resolution of our spectrometer, we discovered standing spin waves in addition to the well known uniform spin wave mode. We have performed a systematic study of these standing spin waves as function of layer thickness for fcc Co films deposited on Cu(100). By comparing the dispersion of the standing mode and the uniform mode dispersion to theory, we obtain information on the layer dependence of the exchange coupling constants.

Wave packets of spin waves offer the unique capability to transport a quantum bit, the spin, without the transport of charge or mass. In this context, large wave-vector and high-energy spin waves are of particular interest as they permit a spin confinement within a few nanometers. Stimulated by the development of advanced electron energy loss spectrometers a considerable number of experimental studies concerning large wave-vector / high-energy surface spin waves of 3d-metal films have emerged lately. These studies were accompanied, partly even anticipated by considerable effort in theory aiming at the understanding of localized spin waves in thin films of itinerant magnets and at the description of inelastic electron scattering from such excitations. In accordance with the surface sensitivity of low energy electron spectroscopy experimental studies focused on the spin waves localized at surfaces and on spin waves in 1-2 monolayer (ML) thick films.

Using our recently developed spectrometer in Jülich, we showed that the power of electron energy loss spectroscopy (EELS) reaches far beyond the study of surface spin waves as such. By virtue of the finite penetration depth of low energy electrons, spin waves localized at interfaces between a substrate and a thin capping layer may be studied yielding information about the exchange coupling between atoms at the interface. An example is discussed in section 1. The quantization of spin waves with wave vectors perpendicular to the film gives rise to standing modes to which EELS has likewise access. Such studies when carried out as function of the film thickness again yield information on the layer dependence of the exchange coupling (section 2). An unresolved issue is the energy dependence of the probability for inelastic scattering from spin waves. For the systems investigated so far, this probability shows a peak at low energies and all spin wave spectra have been obtained in this energy range. This issue is discussed in Section 3.

Spin waves localized at interfaces. Electrons of very low energy have a mean free path that is large enough to penetrate a thin capping layer deposited onto a magnetic film. This permits a unique experimental access to the spin waves localized at the interface between the magnetic thin film and the capping layer. In this context, we have studied the spin waves localized at the nickel/cobalt and copper/cobalt interface [1]. As an example Fig. 1 shows a series of energy loss spectra of spin waves with wave vector q||=0.7A-1 as function of the thickness of the Ni-capping layer. The continuous intensity decrease with the thickness is in quantitative agreement with mean free path of electrons in Ni. The energy of the spin wave decreases upon deposition with a capping layer showing that the exchange coupling between the cobalt atoms is reduced upon capping. The same result is obtained for capping with copper.

Standing modes in thin films. Standing spin waves in thin films arise from the quantization of the perpendicular component of the wave vector. In other words the standing modes have nodes inside the film. In the limit of small wave vectors parallel to the surface q||, the lowest spin wave mode with no node is a uniform mode. In this mode, all spins in the film precess in phase. At larger wave vectors q||, this mode becomes localized to the surfaces of the film and is therefore referred to as the surface mode. The surface mode also exists as a defined excitation on the surface of a bulk system. The first standing wave mode has one node in the center of the film. For larger q|| this mode can be viewed as anti-symmetric combination of the two surface modes at either surface of the film. For higher q|| its frequency merges with that of the surface mode if
the coupling constants are uniform across the film. In that case the energy loss spectrum is actually composed of the surface mode and the first standing mode to an equal weight. Since it is only at low q1 that the surface mode and the first standing mode appear at different energies, observation of the standing modes is very difficult. High energy resolution is required in combination with high sensitivity as realized only by the latest generation of spectrometers. The first observation of a standing mode was reported in 2012 [2]. We have recently performed a systematic study of the surface and the standing modes as function of the film thickness for cobalt layers on Cu(100) [6]. Some sample spectra are shown in Fig. 2.

![Figure 2](image1.png)

**FIG. 2:** High resolution spin wave spectra of five and six layers of fcc cobalt on Cu(100) showing the surface spin wave and the first standing mode.

![Figure 3](image2.png)

**FIG. 3:** Dispersion of the surface mode (open symbols) and the standing mode (solid symbols) as function of cobalt film thickness. The solid and dashed lines are the standing modes and the surface modes, respectively calculated with the coupling constants of Bergqvist et al.

Figure 3 shows the dispersion of the modes in the relevant range of small wave vectors for films consisting of 5-8 layers. Within the limits of error, the dispersion of the surface mode is independent of film thickness whereas the dispersion of the standing mode varies strongly with the thickness. The experimental data are compared to dispersion curves generated within the Heisenberg model using nearest and next-nearest exchange coupling constants published by Bergqvist et al. [7], reduced to 85% of their published value. A good agreement between experiment and theory is observed providing crucial information about the layer dependence of the exchange coupling constants.

**Inelastic scattering from spin waves**

Already in the early work on inelastic electron scattering from spin waves it was observed that the intensity of the spin wave signal depended strongly on the electron energy [3]. The intensity peaked around 6 eV impact energy and vanished completely at higher energies. Since we have now a spectrometer available which is calibrated in terms of the accepted solid angle and the transmission probability we are in a position to convert experimental data on intensities into probabilities for each electron to be inelastically scattered by a spin wave. This is the relevant quantity considered in theory of inelastic scattering [4].

![Figure 4](image3.png)

**FIG. 4:** Probability for inelastic scattering of electrons by spin waves on fcc cobalt films in both high symmetry directions.

An example of an intensity measurement is shown in Fig. 4. The data shows a strong peak at low energies with some fine structure in it. A similar resonance behavior is also observed for hcp cobalt films deposited on Cu(111) [5]. This resonance behavior, by analogy to similar resonances in phonon scattering may be attributed to image potential resonances [5]. However, a quantitative theory of the phenomenon applicable to spin waves is lacking.


Accessing 4f-states in single-molecule spintronics

S. Fahrendorf¹, N. Atodiresei², C. Besson³, V. Caciuc², F. Matthes¹, S. Blügel², P. Kögerler³, D. E. Bürgler¹, and C. M. Schneider¹

¹ Peter Grünberg Institut-6, Forschungszentrum Jülich, Germany
² Peter Grünberg Institut-1 and Institute for Advanced Simulation-1, Forschungszentrum Jülich, Germany
³ Institute of Inorganic Chemistry, RWTH Aachen University, Germany

Magnetic molecules are potential functional units for molecular spintronic devices. However, their magnetic and electronic properties depend critically on their interaction with metallic electrodes. Charge transfer and hybridization modify the electronic structure and thereby influence the molecular magnetic moment. Yet, detection and manipulation of the molecular spin state by means of charge transport mandates a certain level of hybridization of the magnetic orbitals with electrode states. Here we show how a judicious choice of the molecular spin centers determines these critical molecule-electrode contact characteristics. In contrast to late lanthanide analogues, the 4f-orbitals of single NdPc₂ molecules adsorbed on Cu(100) can be directly accessed by scanning tunneling microscopy. Hence, they contribute to charge transport, whereas their magnetic moment is sustained as evident from comparing spectroscopic data with ab-initio calculations. Our results showcase how tailoring molecular orbitals can yield all-electrically controlled spintronic device concepts.

Molecular spintronics combine the auspicious characteristics of molecular electronics and spintronics to exploit the rich diversity and functionality of molecules and the spin degree of freedom for novel nanoelectronic device concepts. An effective approach to molecular spintronics is the investigation of discrete magnetic molecules in contact with metallic leads. In this context, lanthanide (Ln)-based bis(phthalo-cyaninato)-Ln(III) complexes (LnPc₂) represent a promising class of stable and redox-active molecules. However, the 4f-electrons in the late Ln, such as Tb or Dy, lie deep in energy and are spatially localized around the nucleus and, thus, do not contribute to charge transport. Access to the 4f-states in charge-transport experiments require them to be closer to the Fermi level and less localized so as to hybridize with the molecular orbitals of the ligands, all of which are met only for the early Ln. Here, we present the results of a combined experimental and theoretical study of NdPc₂ adsorbed on the Cu(100) surface, a successful model system for a molecule-electrode contact with accessible spin-polarized 4f-states [1]. In contrast to e.g. a Tb³⁺ ion, the Nd³⁺ ion has a larger ionic radius with more delocalized 4f-electrons and, thus, stronger hybridization with the Pc ligands. Thereby, the 4f-orbitals become accessible to transport experiments, while largely maintaining the relative energetic positions of spin-up/down states and consequentially the magnetic moment.

The approximately D₁₇ᵥ-symmetric double-decker structure of the NdPc₂ molecule is shown in Fig. 1(a). One of the two Pc ligands chemisorbs the molecule in a flat geometry on the Cu(100) surface, whereas the second Pc, exposed to vacuum, retains its molecular type electronic features. Figure 1(b) shows a scanning tunneling microscopy (STM) image of a NdPc₂ molecule on Cu(100) and (c) the corresponding calculated STM image.

FIG. 1: (a) Geometry and adsorption configuration of NdPc₂ on Cu(100). (b) STM topography (V₀=-0.8 V, I=2 nA) of an NdPc₂ molecule on Cu(100) and (c) the corresponding calculated STM image.
The hybrid NdPc$_2$/Cu(100) electronic states are explored by performing d/dV measurements at the center of the molecule and above the organic ligand [Fig. 2(a)]. Both spectra display two clear features, one below and one above the Fermi energy $E_F$. For the interpretation of the experimental d/dV spectra and the calculated projected density of states (PDOS) in Fig. 2, it is important to understand first the electronic structure of the free neutral NdPc$_2$ molecule. A total of three electrons, two 6s-electrons and one 4f-electron, are formally transferred from the metal to the ligands, leading to an electrostatic interaction between Nd$^{3+}$ and the two negatively charged Pc rings. As a consequence, the Nd$^{3+}$ ion remains with three 4f-electrons in one spin channel, whereas the two Pc ligands share one unpaired electron.

Spin-polarized first-principles calculations for the adsorbed NdPc$_2$ on Cu(100) in Fig. 2(b) show for the lower Pc ring (green) broad hybrid molecule-surface electronic states due to hybridization and charge transfer, causing the magnetic moment on the ligands to vanish. The PDOS of the upper Pc ring (blue), however, keeps sharp molecular-like features similar to those obtained for NdPc$_2$ in the gas phase and only reproduces the experimental curve, if the electric field due to the bias voltage between tip and sample is taken into account [1]. The striking difference between the two Pc rings suggests that they are coupled via weak hybridization with the three Nd 4f-electrons. This weak hybridization together with Hund's rule constrains the Nd$^{3+}$ 4f-electrons to be in the same spin channel, resulting in the spin magnetic moment. Therefore, the d/dV peak measured on the center site of the molecule (orange) for $V_{bias}=0.8$ V can be unequivocally assigned to an occupied electronic state with mainly 4f-character in the spin-down channel at the Nd site. The d/dV shoulder measured for $V_{bias}=+1.25$ V perfectly matches the calculated PDOS for the unoccupied Nd spin-down 4f-states at the same energy. As a result, in contrast to previously studied late LnPc$_2$ complexes [2,3], the Nd 4f-states can directly be accessed by STM. Similarly, we obtain good agreement between the experimental d/dV spectrum measured at the ligand site (grey) with sharp PDOS features of the upper Pc ring (blue).

A direct contribution of the 4f-states to the tunneling current is further evidenced by the remarkable agreement between the experimental and simulated topography images as well as the corresponding d/dV maps shown Fig. 3. Topography images correspond to isosurfaces of the local density of states integrated over all states between $E_F$ and $eV_{bias}$, rendering simulated topography images rather robust. In contrast, the d/dV maps represent only very few states in a narrow energy interval and, thus, are highly susceptible to small changes to relevant states. Note that the simulated d/dV maps are evaluated at the isosurface of the corresponding topography image without further adjustments. Hence, our conclusions are based on the simultaneously achieved good agreement for both topography images and d/dV maps confirming that the 4f-states, which according to the calculated spin-resolved PDOS curves carry the spin magnetic moment, contribute to the transport through the molecule.

In conclusion, in contrast to extensively studied analogous systems comprising late lanthanides [2,3], the spin-polarized 4f-states are directly involved in electrical transport through NdPc$_2$ molecules in contact with a Cu(100) surface [1]. Accessing these states by means of transport is expected to be a general feature of early Ln-based molecular magnets. Our results open up prospects for electrical manipulation and detection of the molecular spin state, providing the foundation for all-electrically controlled device concepts in molecular spintronics.

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Pyrochlore magnets have attracted intensive attention in the study on geometrical spin frustration and still hold surprises for exotic magnetic ground states, where new intriguing phases arise. Neutron scattering is essential to give a deep understanding of the complicated magnetic behaviour of frustrated magnets. Our research on the pyrochlore antiferromagnet Na$_3$Co(CO$_3$)$_2$Cl reveals a unique coexistence of long-range magnetic order at 1.5 K, an intermediate partial order at 17 K, and a spin-glass-like transition at 4.5 K. Neutron powder diffraction on SPODI identifies a chemically-ordered cubic structure of the sample. The polarized neutron scattering on DNS confirms an all-in-all-out type of long-range magnetic order below 1.5 K. The short-range spin correlations measured on DNS can be well modeled by dominating antiferromagnetic coupling between nearest neighbors and weak ferromagnetic coupling between next nearest neighbors. Inelastic neutron scattering measurements on TOFTOF show spin-wave-like excitations at 3.7 K, indicating that the spin-glass-like transition at 4.5 K is unconventional.

The pyrochlore magnets have been attracting intensive attention in the study on geometrical spin frustration and still hold surprises for exotic magnetic ground states, such as spin glasses, spin liquids and spin ices. New intriguing phases have been discovered in pyrochlore magnets. Magnetic monopoles were found to exist in the spin ice dysprosium titanate (Dy$_2$Ti$_2$O$_7$) with the highly frustrated pyrochlore lattice [1]. Evidence of a Higgs transition from a magnetic Coulomb liquid to a ferromagnet was observed in a pyrochlore magnet Yb$_2$Ti$_2$O$_7$ using polarized neutron scattering [2]. In antiferromagnetic pyrochlores, the high ground-state degeneracy could be lifted by the “order by disorder” mechanism and the perturbations from further neighbour interactions, resulting in complicated magnetic behaviour. Although the commonly accepted wisdom assumes that the formation of a spin-glass phase requires both chemical disorder and frustrated interactions, spin-glass-like behaviour has been detected to the surprise of solid state physicists in a few examples of pyrochlore magnets which are periodic, chemically ordered within the sensitivity of diffraction methods. The origin of this spin-glass-like behaviour has not yet been understood.

Herein, we report an extensive investigation of a spin-frustrated compound Na$_3$Co(CO$_3$)$_2$Cl whose magnetic Co$^{2+}$ ions form a pyrochlore lattice and the nearest neighbors are antiferromagnetically coupled. The Curie-Weiss temperature is about -33.8 K. The temperature dependence of DC magnetization and AC susceptibility measurements show that the system undergoes a spin-glass-like transition at around 4.5 K and a clear collective magnetic behavior at around 17 K. The specific heat measurement down to 60 mK reveals a long-range magnetic phase transition at 1.5 K [3].

FIG. 1: Experimental (Yobs), calculated (Ycalc), and difference (Yobs-Ycalc) NPD patterns obtained at (a) 3.7 K and (b) 30 K with the Rietveld refinement. The green short lines indicate the positions of the Bragg reflections. (c) Difference pattern between the data for 3.7 and 30 K.
To confirm the crystal structure more precisely and detect possible defect structures, we performed neutron powder diffraction (NPD) on SPODI at MLZ within the temperature range 3.7 - 300 K. The experimental NPD patterns for 3.7 and 30 K are shown in FIG. 1 together with the Rietveld refinement with space group F d 3. Satisfying refinement is obtained without introducing any magnetic contribution. No clear evidence for atomic disorder has been found within the resolution of SPODI.

Diffuse neutron scattering with polarization analysis was performed on DNS at MLZ to detect short-range spin correlations and long-range magnetic order in Na₃Co(CO₃)₂Cl. The nuclear coherent, spin-incoherent and para-magnetic scattering contributions were separated unambiguously with the xyz-polarization method. FIG. 2 shows the differential magnetic cross section dσ/dΩ extracted at various temperatures. There is no trace of long-range magnetic order down to 3.3 K, consistent with the NPD measurements. At 50 mK, long-range magnetic order is evidenced by clear magnetic Bragg peaks superposed on the magnetic diffuse scattering. Symmetry analysis based on representation theory shows that the magnetic representation for Co²⁺ spins on 16c site can be described by an all-in-all-out spin configuration (see the inset of FIG. 2), where the spins in one tetrahedron direct either towards or away from the center of the tetrahedron. In FIG. 2 the magnetic reflections observed at 50 mK are fitted within this all-in-all-out spin model.

\[
\frac{d\sigma_{\text{mag}}}{d\Omega} = \frac{2}{3} S^2 (S+1) \left( \frac{m^2 c^2}{\hbar^2} \right)^2 f^2(Q) + \left( \frac{m^2 c^2}{\hbar^2} \right) f^2(Q) \times \sum_{n=1}^{N} C_n \left[ \sin(Q_{fn} - \Omega) + \left( 2A_n - B_n \right) \sin(Q_{fn} - \cos(Q_{fn}) \cos(Q_{fn}) + \cos(Q_{fn}) \right] .
\]

The best fit was achieved when introducing dominating antiferromagnetic nearest-neighbor interactions and weak ferromagnetic next-nearest-neighbor interactions. The fitting results of the short-range spin correlations and the magnetic reflections are plotted as the blue line in FIG. 2.

The spin dynamics of Na₃Co(CO₃)₂Cl was explored by means of time-of-flight inelastic neutron scattering on TOFTOF at MLZ. FIG. 3 shows the contour plot of the dynamic structure factor S(Q, ω) at 3.5 and 15 K. The Q-dependence of the scattering intensities indicates a modulation around the magnetic form factor and thus should be of magnetic origin. Spin-wave-like excitations can be seen centered at around 0.9 Å⁻¹ at 3.5 K by comparing the low-Q regions for 3.5 K and 15 K, which indicates that the spin-glass-like transition at 4.5 K is not a conventional spin glass transition.

An analytical simulation of short-range spin correlations of Na₃Co(CO₃)₂Cl was carried out by attempting a least-square fit to the measured magnetic scattering cross section with the following Fourier transform of spin-pair correlation function,

FIG. 2: Temperature evolution of the differential magnetic cross section. The x- and y- axis correspond to the data for 200 and 300 K. The data for other temperatures are displaced vertically by 0.2 b·sr⁻¹ per Co atom for clarity. The blue line is the best fit to the magnetic scattering at 50 mK based on the all-in-all-out spin configuration. Inset: Schematic representation of the all-in-all-out spin configuration of Co spins in the low temperature pyrochlore phase.

FIG. 3: Contour plot of the dynamic structure factor S(Q, ω) of Na₃Co(CO₃)₂Cl at 3.5 and 15 K.

In conclusion, by means of extensive experimental investigations, we have revealed a novel coexistence of a long-range magnetic order, an intermediate partially-ordered magnetic phase, and a spin-glass-like transition, in one antiferromagnetic pyrochlore, Na₃Co(CO₃)₂Cl. This new model system of pyrochlore magnet certainly deserves more experimental and theoretical investigations to give a deeper understanding to its complex magnetic behavior.

Studying magnetic domains in ferromagnetic alloys and multilayers using soft X-ray scattering

C. Weier\textsuperscript{1}, R. Adam\textsuperscript{1}, D. Rudolf\textsuperscript{1}, A. Kákay\textsuperscript{1}, D. Bürgler\textsuperscript{1}, R. Frömter\textsuperscript{2}, J. Bach\textsuperscript{2}, B. Beyersdorff\textsuperscript{2}, K. Bagschik\textsuperscript{2}, G. Winkler\textsuperscript{2}, A. Kobs\textsuperscript{2}, L. Müller\textsuperscript{3}, S. Schleitzer\textsuperscript{3}, M. H. Berntsen\textsuperscript{3}, P. Grychtol\textsuperscript{4}, H. P. Oepen\textsuperscript{2}, H. C. Kapteyn\textsuperscript{4}, M. M. Murnane\textsuperscript{4}, and C. M. Schneider\textsuperscript{1}

\textsuperscript{1} Peter Grünberg Institut-6, Forschungszentrum Jülich, Germany
\textsuperscript{2} Institut für Angewandte Physik, Universität Hamburg, Germany
\textsuperscript{3} DESY, Hamburg, Germany
\textsuperscript{4} Department of Physics and JILA, University of Colorado and NIST, Boulder, CO, USA

Recent optical pump-probe experiments on magnetic multilayers and alloys pointed out the crucial role of spin superdiffusion in femtosecond magnetization dynamics. It has been demonstrated that superdiffusive spin currents can flow perpendicular to a magnetic thin film \cite{1-3} as well as in lateral direction between magnetic domains \cite{4}. We use synchrotron radiation for analysing coupled magnetic alloys of CoPd and FePd with resonant magnetic scattering (RMS), allowing a comparison of the perpendicular and lateral spin superdiffusion in pump-probe experiments. An element-selective analysis of the scattering images provides a deep insight into magnetic properties of the samples on the nanometer scale. Furthermore, we discuss the feasibility of performing an RMS experiment with a tabletop light source driven by laser-based high-order harmonic generation (HHG) and show the influence of an intense laser exposure on the RMS patterns.

A good understanding and control of magnetic domain structures requires an experimental technique that can image magnetic domains with nanometer lateral resolution. This can be achieved by elastic resonant magnetic scattering of soft X-rays in transmission. The RMS signal originates from X-ray magnetic circular dichroism (XMCD) and allows for detailed studies of magnetic domain patterns with element contrast due to the resonant enhancement of the XMCD signal at the L\textsubscript{3} absorption edges of 3d ferromagnets. Recently, it has been proven that RMS can be used to investigate the dynamics of domains with femtosecond time and nanometer spatial resolution \cite{4}.

We designed and studied CoPd and FePd alloys and coupled CoPd/FePd double layers that will help to further improve our knowledge about ultrafast demagnetization in element-selective RMS experiments. The typically 50 nm thick magnetic films with perpendicular anisotropy were grown by molecular beam epitaxy on 50nm thin Si\textsubscript{3}N\textsubscript{4} substrates to permit soft X-ray measurements in transmission geometry. The first step to a better understanding of the magnetic properties is a static examination using RMS, which is ideally suited to analyse the coupling of two adjacent domain patterns.

The RMS experiments were performed at the P04 beamline of the synchrotron PETRA III (DESY, Hamburg) with circularly polarized X-rays \cite{5} and the data were recorded with a charge coupled device (CCD) camera. Magnetic force microscopy (MFM) images of the CoPd film display stripe domains with a domain width of about 70 nm (Fig.1(a)). The scattering images for a CoPd and an FePd film are shown in Fig. 1(b) and (c). A comparison of the scattering signals at the Fe and Co resonances for a coupled system of FePd and CoPd is given in (d). The scattering vectors of the first diffraction order \(Q_{max}\) are indicated in the images.

FIG. 1: MFM image of a CoPd film (a). RMS images taken from a CoPd film at the Co L\textsubscript{3}-edge (778 eV) and from an FePd film at the Fe L\textsubscript{3}-edge (707 eV) are shown in (b) and (c). A comparison of the scattering signals at the Fe and Co resonances for a coupled system of FePd and CoPd is given in (d). The scattering vectors of the first diffraction order \(Q_{max}\) are indicated in the images.
momentum transfer vector $Q_{\text{max}}$ and implies that the magnetic domains are smaller for this alloy. The average domain periodicity $d$ is related to $Q_{\text{max}}$ by $d = 2\pi / Q_{\text{max}}$ and yields a domain width of about 50 nm for the FePd and about 77 nm for the CoPd layer. The orientation and the shape of the scattering images reflect the average arrangement of the magnetic domains, which strongly depends on the magnetic history and the external magnetic field.

In Fig.1(d) we present RMS data from a double layer system, containing CoPd grown on top of FePd. The similarity of the RMS images recorded at the Fe and Co edge demonstrates the magnetic coupling between the layers. A detailed analysis of Fig.1(b) and (d) shows that the CoPd domain pattern is projected into the FePd film.

In addition to the RMS measurements, carried out with synchrotron radiation, we showed that magnetic domain patterns can be studied with femtosecond extreme ultraviolet (XUV) pulses created by a laser-based HHG source. For this purpose Co/Pt multilayer films have been fabricated by magnetron sputtering. Figures 2(a) and (b) show MFM images for an as-grown Co/Pt sample S1 and for an identical sample illuminated with focused laser pulses reaching a fluence of 0.2 J/cm$^2$ (sample S2). The out-of-plane oriented domains in sample S1 are randomly arranged in a maze-like pattern with an average domain size of about 100 nm. The laser illumination of sample S2 substantially changes the domain pattern that now consists of a set of very large (~2 µm) and small (~100 nm) domains [Fig. 2(b)]. Furthermore, atomic force microscopy reveals that laser-sputtered material re-deposits on the sample surface in the form of nanometer sized droplets (not shown).

The MFM studies demonstrate that the intense laser illumination can introduce permanent fluence-dependent changes, which can be caused by laser sputtering, alloying, melting or interdiffusion.

The scattering image of sample S1 shows the feasibility of RMS studies employing a HHG source [Fig.2(c)]. The image recorded for sample S2 is dominated by charge scattering caused by the re-deposited droplets, which leads to the intense scattering signal at smaller $Q$ values [Fig.2(d)].

The observed laser-induced magnetic structures may also occur in time dependent investigations, if the laser power is close to the sample ablation threshold. Our results demonstrate the importance of the insight gained by the obtained RMS images, which point out the significant influence of the charge scattering contribution.


Magnetic Hardening Induced by Non-Magnetic Organic Molecules

M. Callsen, V. Caciuc, N. Kiselev, N. Atodiresei, and S. Blügel
Peter Grünberg Institut-1 and Institute of Advanced Simulation-1, Forschungszentrum Jülich, Germany

The adsorption of non-magnetic π-conjugated organic molecules on a ferromagnetic surfaces locally increases the strength of the magnetic exchange interaction between the magnetic atoms binding directly to the molecules. This magnetic hardening effect leads to the creation of local molecular mediated magnetic units with a stable magnetization direction and an enhanced barrier for the magnetization switching as compared to the clean surface. Remarkably, such hybrid organic-ferromagnetic systems exhibit also a spin-filter functionality with sharp spin-split molecular-like electronic features at the molecular site. Even more interestingly, depending on the specific molecular structure and ferromagnetic substrate, a strong decoupling of the molecular mediated magnetic units with respect to the magnetic electrode occurs (magnetic softening) and can be successfully used in building spintronic devices that work close to room temperature.

The target of molecular electronics is to employ organic molecules as functional units in electronic devices i.e., as molecular wires, diodes, molecular switches and transistor-like devices. In practice, these devices rely on the electron charge degree of freedom by manipulating the electronic properties of the hybrid molecule-substrate system. Furthermore, the prospect of integrating the electron spin degree of freedom into molecular-based electronic devices leads to the emerging field of molecular spintronics.

We explored the possibility to construct a spintronic device starting from a ferromagnetic surface by locally embedding magnetic units created after the adsorption of a non-magnetic organic molecule, which also exhibits a spin-filter functionality with sharp molecular-like electronic features at the molecular site. Ideally, this molecule should be chemisorbed on the magnetic substrate such that the molecule-metal interaction can locally modify the magnetic properties of the magnetic surface atoms leading to an organic-based magnetic unit.

The challenge imposed by such a hybrid organic-magnetic system is to recognize that an organic molecule chemisorbed on a magnetic surface forms near the Fermi energy broad hybrid molecule-surface bands which, however, can be locally spin unbalanced [1]. In contrast, a well defined spin-filter functionality requires sharp molecular-like electronic states, which can be obtained in the case of a physisorbed molecule.

To reconcile these two contradicting requirements, we theoretically advocate non-magnetic organic molecules with a bi-planar structure of π-conjugated carbon bonds chemisorbed on a magnetic substrate where both (1) a local molecular-based magnetic unit is formed and also (2) a spin-splitting of sharp molecular-like features is present.

As a proof of principle, the adsorption of a single bi-planar π-conjugated electronic structure that forms a 3D π-aromatic network like 2,2-paracyclophane (PCP) molecule (C_{16}H_{16}) on a magnetic Fe/W(110) substrate is a specific example where both effects are found [2].

A key result of our study is that the value of $J_1 = 15.65 \text{ meV}/\mu_B$ describing the magnetic interactions between the Fe atoms underneath the PCP molecule (see Fig. 1) is significantly larger than that for the clean surface atoms $J_S = 5.42 \text{ meV}/\mu_B$. As a consequence, the PCP and the four Fe atoms directly underneath can be regarded as a local molecular-based magnetic unit embedded within the ferromagnetic surface. It is also important to note that for this hybrid system the $J_2 = 5.84 \text{ meV}/\mu_B$ and $J_3 = 5.17 \text{ meV}/\mu_B$ between the Fe atom underneath the molecular unit and the neighboring atoms are slightly larger and slightly smaller than $J_S$, which reveals the locality of the magnetic hardening and a complex magnetic interaction pattern between the local PCP-based magnetic unit and the surrounding ferromagnetic surface atoms. Interestingly, this behavior is

FIG. 1: (a) The side and top view of the hollow site ground-state adsorption geometry of a single PCP molecule on the ferromagnetic Fe/W(110) surface. (b) Top view and magnetic moments of the clean Fe surface atom and the four Fe atoms that chemically interact with the lower ring of the PCP molecule.

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opposite to that unveiled for other π molecular-based magnetic unit on a Co surface, where a strong decoupling of the molecular magnetic unit with respect to the magnetic substrate took place [3].

As an additional remarkable feature, it is important to note that the PDOS of the upper π-ring atoms at the vacuum interface presents sharp molecular-like features (see Fig. 2). This implies that the non-magnetic PCP molecule adsorbed on the ferromagnetic Fe/W(110) surface acts as a molecular spin filter [4] although after absorption the molecule remains non magnetic.

Furthermore, we explores the consequences of the strong impact of the hybrid organic-metallic states formed at the interface on the macroscopic magnetic properties of the hybrid system, we performed simulations for a magnetization reversal process at finite temperature using Monte Carlo (MC) method. As depicted in Fig. 3(a), at a fixed temperature the simulated magnetization curves provide an estimate of the coercivity field $H_C$ required to switch the magnetization of the molecule-surface system. The most important outcomes of the MC investigations are the increase of the Curie temperature by 27 K and an increase of the coercivity field $H_C$ below ordering temperature for a clean (squares) and PCP covered (triangles) magnetic Fe monolayer. Solid lines in (b) result from a linear fit of the $H_C$ as function of temperature. The Curie temperatures are $T_C = 165$ K and $T_C = 192$ K for the clean and PCP-covered Fe/W(110) surface, respectively.

This molecular induced local magnetic hardening is a result of the hybridization between the π-molecular orbitals of the lower PCP ring with the π-structure of the magnetic interface that leads to increased exchange interactions and a larger magnetic anisotropy energy [2], which results in a stable magnetization axis, an increase of the Curie temperature as well as of the magnetic coercivity fields.

In practice, such molecular-based magnetic units can play an important role for memory device applications. We conjecture that the potentially important technological device-like characteristics (i) and (ii) are generic to molecules with a bi-planar structure of π-conjugated carbon bonds, which allows chemisorption on magnetic surfaces and having molecular-type spin-split electronic states of π-orbitals at larger distance from the interface.

The computations were performed under the auspices of the VSR at the computer JUROPA and the GCS at the high-performance computer JUQUEEN operated by the JSC at the Forschungszentrum Jülich.

In summary, our spin-polarized first-principles study demonstrated the possibility to design a hybrid organic-ferromagnet interface system consisting of a non-magnetic organic molecule (PCP) chemisorbed on a magnetic substrate (Fe/W(110)), which (i) all-in-all acts as a local embedded molecular-based magnetic unit due to a magnetic hardening of the substrate and (ii) exhibits simultaneously a spin-filter functionality with sharp spin-split molecular-like electronic features at the molecular site, previously known only for physisorbed molecules.

**FIG. 2:** The projected density of states (PDOS) at the molecular site expressed in terms of the $\sigma$ ($s + px + py$) and $\pi$ ($pz$) type molecular-like orbitals of the lower (a) and the upper (b) ring of the PCP molecule in its ground-state on the Fe/W(110) surface. The lower ring binds to the substrate by chemical bonds and in consequence broad spin-polarized hybrid molecule–surface bands are formed. In contrast, the PDOS for the upper ring shows distinct sharp spin-split molecular-like features.

**FIG. 3:** Results of the Monte Carlo simulations (a) for the magnetization-reversal process at $T = 145$ K and (b) for the coercivity field $H_C$ below ordering temperature for a clean (squares) and PCP covered (triangles) magnetic Fe monolayer. Solid lines in (b) result from a linear fit of the $H_C$ as function of temperature. The Curie temperatures are $T_C = 165$ K and $T_C = 192$ K for the clean and PCP-covered Fe/W(110) surface, respectively.

Signs of ultra-high fragility in phase change materials

M. Salinya and M. Wuttig
I. Physikalisches Institut A, RWTH Aachen University, Germany

Phase change materials are the basis for next-generation memories and reconfigurable electronics, but the fundamental understanding of the unconventional kinetics of their phase transitions has been hindered by challenges in experimental quantification. Deeper insights are gained based on the temperature dependence of the crystal growth velocity of the phase change material AgInSbTe, as it is derived from laser-based time-resolved reflectivity measurements [1]. We observe a strict Arrhenius behavior for the growth velocity over eight orders of magnitude (from \(~10\text{nm/s}\) to \(~1\text{m/s}\)). This can be attributed to the formation of a glass at elevated temperatures due to rapid quenching of the melt. Furthermore, the temperature dependence of the viscosity is derived, which reveals that the supercooled liquid phase must have an extremely high fragility (>100).

So far measurements of crystal growth velocity in phase change materials have been limited to rather low temperatures where crystallization speeds are still slow. It was only very recently that Orava et al. undertook a vast extension of the range of investigated crystallization speeds using ultra-fast differential scanning calorimetry and derived information on the crystal growth velocity. In this study the as-deposited amorphous phase was investigated under non-isothermal conditions [2]. In the past, fast measurements have always been performed in a non-isothermal way employing short laser or voltage pulses to crystallize a small volume of material causing severe difficulties to obtain the temperature dependence of nucleation and growth velocities.

In our lab, we take a new approach to quantify the temperature dependence of the crystal growth velocity. Our laser-based method illustrated in Fig.1 allows the investigation of the technologically relevant melt-quenched amorphous phase under isothermal conditions. Since the crystallization process in AgInSbTe is dominated by growth, even in the ultra-fast regime, as proven by TEM measurements, our laser experiments result in the crystal growth velocity as a function of temperature. For AgInSbTe this is plotted in Fig. 2 for temperatures between 418 K and 553 K. The measured recrystallization times range from several seconds down to some hundred nanoseconds, and correspond to crystal growth velocities spanning eight orders of magnitude from around 100 nm/s at 418 K up to more than 3 m/s at 553 K.

This unprecedented quantitative experimental evidence leads to far-reaching conclusions about the viscosity of the material under investigation, here AgInSbTe, not only in the melt-quenched amorphous solid but also in its supercooled liquid phase.

Although the data in Fig. 2 end at 553 K for experimental reasons, it can be clearly seen that it is not possible to extend the Arrhenius behaviour of the crystal growth velocity up to the melting point (Tm=808K). Assuming this trend, the speed of sound in amorphous AgInSbTe (~1000 m/s) would be overcome at around 625 K. Hence, at higher temperatures, a quite dramatic change in the temperature dependence of the crystal growth velocity must occur. It is reasonable to suspect that the origin of this change is related to the intrinsic characteristics of the disordered phase.

For a comprehensive discussion of the glass dynamics of these alloys, we derive values for the viscosity of AgInSbTe from the measured crystal growth velocities. Fig. 3 clearly shows that the change of the crystal growth velocity over eight orders of magnitude is dominated by the temperature dependence of the viscosity. In contrast, the contribution from the driving force of
crystallization changes only by 26% over the whole temperature range probed.

As for the growth velocity, also for the viscosity the experimentally determined Arrhenius behaviour cannot extend to much higher temperatures, since the viscosity value at around 550 K (~170 mPas) is not even two orders of magnitude away from the viscosity measured in the liquid (~2 mPas). Such a pronounced flattening out of the viscosity (and thereby also of the growth velocity) towards higher temperatures can only be realized if a material's supercooled liquid phase has a fragility as high as 130. Fragilities reported in literature range from 20 for very strong liquids like SiO$_2$ up to over 150 for some very fragile, typically organic polymers (inorganic materials usually show fragilities only up to 90).

![Temperature dependence of crystal growth rate](image)

**FIG. 2.** Temperature dependence of crystal growth rate from [1]. The growth velocity in melt-quenched amorphous AgInSbTe (red circles) has been measured by the laser leafer on a wide range of temperatures probing more than eight orders of magnitude both in the slow and in the ultra-fast crystallization regime. The red pentagon refers to an in-situ TEM recrystallization experiment also reported in [1]. The data exhibits an Arrhenius dependence on temperature characterized by a unique activation energy of 2.7 eV. The new data for melt-quenched amorphous AgInSbTe show much faster crystal growth velocities than what had been observed in as-deposited amorphous AgInSbTe thin films (blue squares) [3]. The maximum speed for melt-quenched AgInSbTe (~100 m/s, red dashed line) has been estimated on the basis of two-pulse experiments also described in [1].

The strong bending of the viscosity-temperature-curve (lines in Fig. 3) that comes with a high fragility is, however, incompatible with the straightness of the experimental data at lower temperatures. This is true even if one takes into account a potential decoupling of the viscosity from the atomic diffusivity ("break-down of Stokes-Einstein relation"). Since our experimental data cannot be described by the theoretical formulae for a supercooled liquid phase, we consequently interpret them as representing a melt-quenched glass for which the atomic configuration deviates from the equilibrium configuration of the supercooled liquid at a rather high temperature due to the vast cooling rates (~10$^{15}$ K/s) employed.

![Temperature dependence of viscosity](image)

**FIG. 3.** Temperature dependence of viscosity from [1]. Viscosity of AgInSbTe as a function of temperature (filled red circles) calculated from the growth velocities in Fig. 2. The general understanding that a glass is formed upon cooling from a supercooled liquid implies that the curves of supercooled liquid (continuous lines) and glass (red triangles) have to connect. The lines (black and red) are obtained by fitting the equation proposed by Mauro et al. [4] for the description of the viscosity of a supercooled liquid to the laser results at the highest measured temperatures together with literature values for the viscosity in the liquid phase. Both fits correspond well with a viscosity of 10$^2$ Pas at the glass transition temperature $T_g=443$K (green filled circle) that was previously observed for AgInSbTe using calorimetry. The blue squares are obtained using the data on as-deposited AgInSbTe reported in ref. 3. The blue diamonds are extracted from a study in which viscosity of AgInSbTe has been measured via mechanical stress relaxation.

The comparison of our measurements of melt-quenched material with data on as-deposited amorphous films (blue data points in Fig. 2 and 3) exhibits a strong discrepancy between the kinetics of these distinct disordered solids of identical composition. This demonstrates how crucial it is to measure the temperature dependence of the growth velocity for the technologically relevant melt-quenched state when aiming for realistic estimates of device performance, e.g. with respect to retention times and switching speeds.

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Tailored Thermoelectric Transport via Disorder Control

I. Physikalisches Institut A, RWTH Aachen University, Germany

The ability to control transport properties is decisive for many applications. A very common approach for instance to tailor electrical properties is via doping, enabling the control of the system’s Fermi level. A complementary and rarely utilized strategy is the control of the disorder of the crystalline solid. Only recently a material system within the class of phase change materials has been identified where electrical transport is governed by pronounced configurational disorder. The control of this disorder therefore allows for an adjustment of transport properties.

The lion’s share of phase change materials (PCMs) are telluride based chalcogenides where both, an amorphous and a crystalline state are stable at ambient conditions. Yet, the phase transition can proceed on a nanosecond time scale. This feature together with the fact that these two states differ significantly in their physical properties, such as reflectivity or resistivity, makes PCM highly suited for non-volatile data storage [1].

This very class of materials is not only famous for its rapid phase transition. In fact, prominent PCMs like GeTe are isoelectronic or even alloyed in well-established thermoelectrics (TE) such as PbTe or TAGS [(GeTe)0.5(AgSbTe2)0.5]. Although these are very different applications they share some fundamental requirements that are met by these alloys. For example a low lattice thermal conductivity in PC-RAM is crucial to confine the generated Joule heat in the PC cell. In thermoelectric applications this is mandatory to maintain the temperature gradient along a TE device. Fortunately these alloys exhibit intrinsically low lattice thermal conductivities which was only recently attributed to the underlying bonding mechanism (resonant bonding) that gives rise to strong anharmonicity [2]. Moreover it is decisive to tailor electronic properties in both applications. In PC-RAM, for instance, a fairly high resistance in the crystalline state (but still small enough to be well separated from the amorphous value) facilitates a low power reset operation. In TE a concerted variation of the carrier concentration (e.g. the system’s Fermi level) is used to meet the trade-off between high electrical conductivity and high thermopowers. Recently, we have compiled our results on tailoring electronic as well as thermoelectric properties solely by the alloy’s degree of disorder [3].

The materials investigated are compounds based on Ge, Sb and Te. Alloys like Ge2Sb2Te5 or Ge6Sb2Te11 were already exploited in optical data storage (e.g. DVD-RW). They can be understood as a pseudo-binary compound of GeTe and Sb2Te3 (figure 1). For instance, Ge1Sb2Te4 is GeTe:Sb2Te3 (50:50), or (GeTe)1-x(Sb2Te3)x, x=0.5. These materials develop a stable hexagonal structure, which in case of Ge1Sb2Te4 consist of layered building blocks of Te-Sb-Te-Ge-Te-Sb-Te. These building blocks are separated by van-der-Waals gaps, like in Sb2Te3 or Bi2Te3, respectively. Additionally most of these alloys can be crystallized in a meta-stable rock-salt like phase that is highly disordered. Here the anion site is occupied by tellurium. By counting the number of anions and cations, we find that in Ge1Sb2Te4 we have only 3 cations (Ge, 2xSb) as compared to 4 Te anions. Since there is no evidence for phase segregation of Te in this cubic phase, an amount of 25% of stoichiometric vacancies must be present on these anion sites. In fact, these vacancies within the cubic structure are necessary to make up the van-der-Waals gaps in the stable hexagonal phase. To account for these stoichiometric amount of vacancies, one may rewrite the structure formula as (GeTe)1-x (□:Sb2Te3)x, where □ represents the vacancy. From this it is evident that the fraction of stoichiometric vacancies changes with x as x/(1+2x). These vacancies are not pinned to fixed lattice sites (unlike in defective chalcopyrites for instance) but distributed randomly. The importance of these vacancies in terms of chemical stability is also discussed in [4].
FIG. 2: Electric transport properties in differently annealed Ge$_3$Sb$_2$Te$_6$ and Ge$_8$Sb$_2$Te$_{11}$ films. Annealing allows for adjusting electronic properties [3].

Using DFT calculations Zhang et al. identified clusters of vacancies to cause electronic localization in this highly disordered meta-stable cubic phase [5]. This is accompanied by thermally activated charge transport (i.e. hopping). Via annealing it is possible to reorganize the cation site which finally drives the transition to the stable hexagonal phase. This ordering process within the cubic state promotes the dissolution of vacancy clusters which triggers the transition from an insulating to metallic state as reported by Siegrist et al. [6].

Recently we have explored the thermoelectric potential of Ge$_3$Sb$_2$Te$_6$ (GST326) and Ge$_8$Sb$_2$Te$_{11}$ (GST8211). The thin-films, produced using DC magnetron sputter deposition, were amorphous as deposited. Afterwards they were crystallized and annealed in a tube furnace at $T_{\text{Anneal}}=200^\circ$C, 225$^\circ$C and 250$^\circ$C, respectively to access different degrees of disorder on the cation site.

Figure 2 shows temperature dependent conductivity, thermopower and power factor ($S^2\sigma$) data. Annealing strongly affects the electrical conductivity, in line with Siegrist et al. [6]. Higher annealing temperatures (less disorder) lead to enhanced conductivity. This of course impacts the thermopower that decreases in absolute values on annealing. In GST326 the increase in $\sigma$ is overcompensated by the reduction in thermopower causing no net effect on the power factor. In GST8211, on the contrary, annealing can be utilized to tailor the power factor to fairly high values of 6 $\mu$Vcm$^{-1}$K$^{-1}$.

Of course disorder is not expected to solely affect electronic degrees of freedom. In fact, the high amount of disordered vacancies serves as efficient phonon scatterers that further reduce the intrinsically low lattice thermal conductivity ($\kappa_{\text{GST8211}}\approx$0.6 Wm$^{-1}$K$^{-1}$, $\kappa_{\text{Sb$_2$Te$_3$}}=1.5$ Wm$^{-1}$K$^{-1}$) [3,7].

The trends in thermo power are mirrored in the thermoelectric efficiencies $ZT= S^2\sigma/\kappa$ (Fig. 3). Due to the very small thermal conductivity, GST8211 can even compete with an established thermoelectric material such as Sb$_2$Te$_3$ and develops enhanced thermoelectric efficiencies at elevated temperatures ($ZT=0.7|T=120^\circ$C) [3].

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[7] K. S. Siegert et al., to be published.
Reversible tuning of mid-infrared antenna resonances using phase-change materials

A.-K. U. Michel, D. N. Chigrin, M. Wuttig, and T. Taubner
I. Physikalisches Institut A, RWTH Aachen University, Germany

Metallic nanostructures can act as “antennas” for light and resonantly enhance optical and infrared near-fields. The spectral positions of the antenna resonances are mainly given by the geometry of the nanostructure and the refractive index of the surrounding medium, thus are usually fixed after their fabrication. Here we show the tuning of the resonance frequency of aluminum nanoantennas via variation of the refractive index $n$ of a layer of phase-change material (PCM). PCM offer a huge index change upon the structural transition from the amorphous to the crystalline state, both stable at room temperature. Ge$_3$Sb$_2$Te$_6$ is chosen as the PCM, since it offers very low losses in the infrared spectral range. Reversible switching of the antenna resonance frequencies is realized by femtosecond laser pulses.

Since metallic nanoantennas have a well-defined, but fixed operation frequency and wavelength, the field of “active plasmonics and nanooptics” has gained tremendous interest in the recent years. A change of the structure’s resonance frequency can be realized either by damping the resonance amplitude or by shifting the position of the resonance frequency. In the infrared spectral range, this was done by changing the refractive index $n$ of the antennas environment, e.g. by electrically changing the carrier concentration of doped indium antimony or graphene and by exploiting the metal-to-insulator transition of vanadium dioxide. However, these concepts are limited by large losses (graphene) and are non-volatile, because the resonance shift only occurs while the raised temperature or applied electric voltage is maintained. We showed recently that antenna devices based on Ge$_3$Sb$_2$Te$_6$ allow non-volatile, low-loss and wide-range tuning of antenna resonances in the mid-infrared spectral range [1].

We use a group of chalcogenides, named phase-change materials (PCMs), to reversibly shift the resonance frequency of infrared nanoantenna arrays, in a non-volatile way. PCMs are temperature stable in at least two structural phases (crystalline and amorphous) and further allow for ultrafast reversible switching between these states. PCMs are typically based on the combinations of the elements germanium, antimony, tellurium and indium and show a pronounced change of their dielectric function $\varepsilon(\omega)$ - and thus the refractive index $n=\sqrt{\varepsilon(\omega)}$ - during the structural phase transition between the amorphous and crystalline states. In the mid-infrared spectral range, PCMs offer a huge contrast in the real part of the permittivity $\varepsilon_1$. Specifically, we use Ge$_3$Sb$_2$Te$_6$ (from here on abbreviated as GST-326) because in the investigated spectral range its refractive index $n$ changes from about 3.58 in the amorphous to about 6.33 in the crystalline phase, while it also exhibits a very small ratio of the imaginary to the real part of the permittivity, i.e. $\varepsilon_2/\varepsilon_1 << 0.1$. This combination of low losses due to small absorption and the huge refractive index change make GST-326 a very promising material in the field of tunable plasmonics and nanooptics as well as for the design of tunable metamaterials.

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FIG. 1: A. Scheme of the sample geometry with a 50 nm PCM thin film covering aluminum nanoantennas (30 nm height) on an chromium adhesion layer. B. The antennas (width $w$, length $L$ and distance $d_C$) are arranged as an array; scale bar 300 nm.

Figure 1A shows a schematic cross-section of an antenna array. Aluminum nanoantennas are fabricated by electron beam lithography and thermal evaporation of the metal on a Silicon substrate. Chromium is used as an adhesion layer.

After fabrication, the antennas arrays are covered with a thin film (50 nm) of amorphous GST-326 via sputter deposition. Figure 1B shows an SEM image of a typical antenna array. The period $d_C$ within the nanoantenna array was optimized to provide constructive interference of the individual antennas, which results in a spectrally narrow collective excitation resonance in the mid-infrared spectral range. The resonance frequency of the antenna array is probed by Fourier-Transform Infrared (FTIR) Spectroscopy and displayed in Fig. 2. The black curve in the top panel of Fig. 2 shows the resonantly enhanced infrared reflectance spectrum for an antenna array with an antenna length $L = 500\text{ nm}$. The resonance position is determined by the antenna geometry and the chosen materials for the antennas, the substrate and the cover layer. Changing the structural phase of the GST-326 cover layer will shift the spectral
position of the antenna array’s resonance, since the permittivity $\varepsilon(\omega)$ of the GST-326 changes. Crystalization leads to an increase of the refractive index of the GST-326 cover layer and thus to shift of the antenna resonances to smaller wavenumbers (or larger wavelengths), as seen by the green curve in Figure 2. The resonance frequency is shifted from position 1 at 2490 cm$^{-1}$ to position 2 at 2200 cm$^{-1}$ after crystallization, which results in a total shift $\Delta \nu = 290$ cm$^{-1}$. To quantify the tuning of the resonance frequency, we calculate a tuning figure of merit (TFOM): The TFOM is the ratio of $\Delta \nu$ to the full width at half maximum (FWHM) of the resonance peak. We achieved values greater than 1 [1], which is an increase of more than factor 2 compared to literature. Note that this initial transition from the as-deposited amorphous (AD, black) to the crystalline (C, green) phase was realized by heating the sample above the crystallization temperature $T_C$ (167°C) of GST-326. The left side of Fig. 3 illustrates this sample treatment. In order to demonstrate reversible switching of the antenna resonances, we continue with laser-induced switching.

The laser switching parameters and achieved phases are schematically displayed on the right hand side of Figure 3. To achieve the reversible switching of the antenna array resonances, we used a femtosecond laser source with 800 nm (12500 cm$^{-1}$) central wavelength. To amorphize the C-GST-326 layer, the crystal lattice has to be heated above the melting temperature $T_M$ (630°C) and subsequently cooled down rapidly (“quenched”) to room temperature to avoid any re-crystallization of the atomic structure. A 50 fs single pulse with a high fluence is sufficient to induce amorphization from C- to MQ-GST-326 phase. The resulting reflection spectrum (orange curve in Fig. 2) shows a resonance peak shift to smaller wavenumbers. However, this shift does not reach the value obtained after the crystallization on a hot plate (green curve in Fig. 2). We attribute this to the influence of the antennas on the re-crystallization behavior. For a better visualization, the lowest panel in Fig. 2 shows the shifts between the resonance frequencies obtained after the various sample treatment steps: the dots labeled with 2, 3 and 4 in Fig. 2 correspond to the fs laser induced switching of the GST-326 thin film covering the antennas [3].

In summary, we have shown reversible optical switching of mid-infrared antenna resonances using a phase-change material and fs-laser pulses. Our concept can be generalized for the reversible switching of more complex antenna structures or even metamaterials. The optical excitation could in future allow to address single antennas to switch them independently, creating new functionalities for active plasmonic devices and reconfigurable metamaterial-based optical elements like filters or polarizers.

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Application of EUV discharge-plasma source for the coherent diffraction imaging metrology

L. Juschkin\textsuperscript{1,2}, L. Loetgering\textsuperscript{2}, D. Rudolf\textsuperscript{2}, R. Xu\textsuperscript{3}, S. Brose\textsuperscript{4}, H. Kim\textsuperscript{1}, J. Bußmann\textsuperscript{2}, S. Danylyuk\textsuperscript{4}, and J. Miao\textsuperscript{3}

\textsuperscript{1} Chair for Experimental Physics of EUV, RWTH Aachen University, Germany
\textsuperscript{2} Peter Grünberg Institut-9, Forschungszentrum Jülich, Germany
\textsuperscript{3} Department of Physics and Astronomy, and California NanoSystems Institute, University of California, USA
\textsuperscript{4} Chair for Technology of Optical Systems, RWTH Aachen University, Germany

The presented experiments explore the feasibility of coherent diffraction imaging (CDI) using bright sources emerged from the technology development of EUV lithography, paving the way for laboratory-scale CDI application. We present here results of lensless imaging experiments performed using a tabletop discharge plasma source of extreme ultraviolet (EUV: 1-50 nm wavelength) radiation. By using a pinhole and different illumination geometries, beams of varying degree of the spatial coherence are generated and utilized to obtain far-field diffraction patterns. These patterns have been used for the iterative reconstruction of an illumination wavefront within a precision pinhole at the object plane.

Decreasing feature size in Nanoscience makes it necessary to shift the wavelength of microscopy to the nanometer-scale. The use of conventional imaging techniques for 1-50 nm radiation is limited due to absorption of the EUV radiation by most optical materials. This makes refractive optics inapplicable; while reflective optics suffer from imperfections of surface topography (e.g. surface figure and finish error, mid-spatial frequency roughness). The use of diffractive optics, e.g. zone plates, is limited due to inability to achieve the required nm-scale in manufacturing so far. Coherent diffraction imaging (CDI) on the other hand, allows achieving the diffraction limited resolution without the drawbacks of conventional optics. CDI is a lensless imaging technique, in which a coherent wave illuminating an object produces a far-field diffraction pattern recorded by a 2D spatially resolving detector. If sufficiently oversampled, the diffraction pattern can be directly phased to obtain the object’s image with a resolution limited only by a quality of the diffraction signal [1]. The well-known phase problem is solved by combining the oversampling method with iterative algorithms [2]. Since the first experimental demonstration in 1999 [1], CDI has been applied widely to image a variety of samples ranging from nanocrystals, nanoparticles, biomaterials, magnetic structures, cells, and cellular organelles to viruses. While CDI has been actively explored across different fields, a major limitation was the availability of coherent x-ray sources, e.g. synchrotrons or x-ray free electron lasers.

![FIG 1: Optical setup of the CDI experiment. The 300 µm aperture is limiting the solid angle between source and sample. Not shown is another optical arm with a grating and CCD sensor for spectroscopy. Detailed information can be found elsewhere [3].](image)

To overcome this limitation, tabletop CDI was developed and demonstrated, reaching these days spatial resolution of 22 nm employing radiation of 13 nm wavelength with high-harmonics laser beams (HHG) [4]. We report on an alternative tabletop CDI experiment using a discharge produced plasma (DPP) EUV source. Although it is a partially coherent source, the coherence can be enhanced further by using appropriate optical elements.
FIG 2: Light spectrum after passing Mo/Al filter. The spectrum has a strong peak at 17.3 nm. The insert shows the transmission function of the Mo/Al filter (small insert: non-logarithmic transmission between 16 – 21 nm).Transmission of the filter is calculated using the data from the Center for X-Ray Optics [6).

FIG. 3: a) Measured diffraction pattern (122 pixel x 122 pixel) of a ~ 10 µm pinhole obtained using radiation from oxygen plasma. b) Result of the OSS reconstruction of the transmission function of the pinhole from the diffraction pattern.

Compared to HHG, the discharge-plasma EUV source is more compact, has better monochromatic output within individual emission lines, and can be more easily implemented. The presenting CDI measurements have been performed with a source realized at the Fraunhofer Institute for Laser Technology (ILT) [5]. The experimental setup is shown in figure 1. The diffraction pattern of the sample is recorded by the Andor iKon-M CCD camera. A spectral bandpass filter (200 nm Al/60 nm Mo) installed in the beam pass is used to select the 17.3 nm line of the oxygen spectrum (the aluminum absorption edge at 17 nm sifts 17.3 nm line of oxygen spectrum, whereas the molybdenum is used to suppress most of the longer wavelength radiation). Figure 2 shows the calculated spectral transmission curve of the Al/Mo filter and the measured spectrum of the source after filtering. Downstream the spectral filter, an aperture of 300 µm size is placed, limiting the effective radiation source size and increasing therefore the spatial coherence. The object used for the first CDI experiments and for the set-up characterization, is a precision pinhole ~ 10 µm size from Edmund Optics. Figure 3a shows a diffraction pattern generated by the pinhole. The data refinement procedure comprises several steps: Background and hot pixel subtraction, binning to increase signal-to-noise ratio and reduce the required computational power during the iterative reconstruction, searching for the center of symmetry and aligning the data accordingly. An OSS algorithm [7] is applied to reconstruct the sample image. 128 independent initial phase estimates are generated and used to run the OSS in a first cycle of 100 iterations. The best 5 reconstructions, measured with the lowest RF factor, which is defined by:

$$ R_F = \frac{\sum_k |F_m| - |F_n|}{\sum_k |F_m|} $$

where $F_m$ is the measured diffraction amplitude and $F_n$ is the calculated one for the reconstructed object after the n° iteration, are chosen for the second cycle of the OSS. The reconstructed image depicted in figure 3b has a diameter of 11.2 µm. From Figure 3b one can clearly see that the aperture was situated at the slope of the Lorentzian illumination profile during this measurement [3]. In this experiment we show a successful application of the discharge plasma-based EUV source for the demonstration of Coherent Diffraction Imaging technique. This is a proof-of-principle demonstration of a possibility to build versatile laboratory-scale CDI devices for scientific and industrial applications. In addition, using specially designed test objects several problems of implementing the DPP source for CDI are identified [3]. These include the requirement of better spectral filtering of longer wavelength in the VUV spectral range as well as in the soft x-ray, e.g. with Parylene-Aluminum system as the presence of emission of several spectral lines in the source spectrum reduces the temporal coherence. This problem may be enhanced also by parasitic transmission through insufficient absorption layers. Coherent photon flux at the image plane is demonstrated on the order of 10^15 photons/s. Narrow bandwidth of resonant emission lines together with the possibility of using emission lines from different working gases and their various ionization states, reveal a potential for realization of the compact laboratory-scale spectral CDI experiments with elemental sensitivity.

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http://henke.lbl.gov/optical_constants/filter2.html
Detection of impure liquids with High-Tc Josephson spectrometers

M. Lyatti\textsuperscript{1,2}, I. Gundareva\textsuperscript{1,2}, A. Snezhko\textsuperscript{1,2}, V. Pavlovskiy\textsuperscript{2}, V. Gubankov\textsuperscript{2}, U. Poppe\textsuperscript{1}, K. Urban\textsuperscript{1}, and Y. Divin\textsuperscript{1,2}

\textsuperscript{1}Peter Grünberg Institute-5, Forschungszentrum Jülich, Germany
\textsuperscript{2}Kotel’nikov Institute of Radio Engineering and Electronics of RAS, Moscow, Russia

Two liquid identifiers have been developed based on quasioptical and waveguide-type high-\textit{T}_c Josephson spectrometers. The frequency bandwidth was of 1 \textendash 300 \text{GHz} and 30 \textendash 500 \text{GHz} for spectrometers with waveguide and quasioptical radiation coupling, correspondingly. Scanning times of 0.2 \textendash 5 sec and measurement error of 0.3\% has been achieved. The results of spectroscopic measurements on liquid samples of various purities and mixtures, including 30\% \textit{H}_2\textit{O}_2/\textit{H}_2\textit{O} and ethanol-water mixtures, are presented.

Among various ways of explosive detection under discussion, the techniques using electromagnetic radiation (i.e. microwave and terahertz imaging and spectroscopy) are considered as having great potential \cite{1}. Liquids, for example, can be reliably, with low rates of false alarms, identified by measuring their electromagnetic responses, i.e. dielectric functions, at the frequency range of their main dispersions and comparing them with reference data. However, the spectral range of dispersion for pure liquids is rather broad, from a few gigahertz (GHz) to a few terahertz (THz), and not covered by any single conventional spectroscopic technique.

Hilbert-transform spectroscopy, which is based on high-\textit{T}_c Josephson detectors, has a broad frequency range from a few GHz to 5 THz, large power dynamic range of 50 \textendash 80 dB and can be used for a quick identification of liquids. To prove this idea a concept of a liquid identifier based on a high-\textit{T}_c Josephson detector has been suggested \cite{2}. The liquid identifier consists of a broadband radiation source, a radiation coupling unit, the Josephson detector and a data acquisition system, controlled by a computer.

Following the concept, two demonstrators of liquid identifier were developed. The first one had a quasioptical coupling unit. In this demonstrator, radiation from a broadband polychromatic source was focused by a gold-plated elliptical mirror on a bottle with liquid, and the radiation, reflected from the bottle, was focused on the Josephson detector controlled by a computer.

The second liquid identifier had a radiation coupling unit based on a dielectric waveguide. The radiation coupling unit based on the dielectric waveguide was used to extend frequency range down to 1 GHz. In this demonstrator, the radiation of the broadband radiation source was directed to the liquid by a polyethylene waveguide, sandwiched between two metal plates, reflected from liquid and guided by another PE waveguide to the Josephson detector. In addition to the frequency multipliers, a frequency synthesizer was added to the radiation source. Such radiation source could deliver the radiation in the frequency range of 1 \textendash 300 \text{GHz}. The detailed description of the experimental setup can be found in \cite{5}.

In both cases, the radiation was analyzed by the Josephson detectors. The detectors were based on YBa_2Cu_3O_7-x bicrystal Josephson junctions integrated in electrically-driven Stirling coolers. The junctions were optimized to ensure the required values of the frequency bandwidth, the power dynamic range and the detection accuracy.

In the quasioptical setup, a voltage across the junction was scanned to get a frequency-selective response, which later was converted into reflected radiation spectrum. The scanning time was of 0.2-5 sec. In the waveguide setup, the measurements were carried out in two steps. At the first step, the output frequency of the frequency synthesizer was swept in the range of 0.7 \textendash 20 \text{GHz} and the broadband detector response was measured at the constant voltage across the junction. The scanning time for low frequency measurements was of 0.05 \textendash 5 sec. At the second step, the detector response on higher frequencies (>50 \text{GHz}) was measured. The measurement procedure and scanning times were similar to that of the quasioptical setup. A measurement error of 0.3\% was achieved for both liquid identifiers.

In our previous works we have successfully demonstrated the possibility to identify a number of pure liquids by our liquid identifiers \cite{4,5}. In this work we have tested liquids identifiers with liquids of various purities including deionized distilled water (18.2 MOhm-cm), distilled water, tap water, ethanol-water mixtures, two types of 30\% \textit{H}_2\textit{O}_2/\textit{H}_2\textit{O} mixtures, \textit{NaCl} and sugar aqueous solutions, various beverages and many other liquids. The deionized distilled water was used as a reference in all measurements. Both liquid identifiers demonstrated the capability to distinguish water-based liquids from other liquids.
FIG. 1: Response of liquid identifier with waveguide coupling on liquids with different purities.

FIG. 2: Response of quasioptical liquid identifier on ethanol-water mixture.

as well as similar water-based sugar-containing and sugar-free beverages, like Cola and Cola Zero [4-8].

The difference between the various types of water was more pronounced at low frequencies (see fig. 1) due to the losses related to an ionic conductivity [6]. The reference response of the deionized distilled water is shown in fig. 1 by a dashed line. The special attention was paid to the measurement of hydrogen peroxide, because hydrogen peroxide is a water-like liquid, a strong oxidizer, which can be used as an explosive or as a component for fabrication of explosives. We could detect the difference between water and 30% H2O2/H2O mixture, which was not constant over the frequency range. The maximum difference of 6.5% was observed at 0.95 GHz (see fig. 1) [6], no difference was found at 32 and 95 GHz, but at 282 GHz the reflectance of 30% H2O2/H2O was by 1.7% higher than the reflectance of water. At the frequency of 470 GHz, the difference between 30% H2O2/H2O and water has increased up to 3.3% [7].

Due to a large difference in relaxation times τ1 for ethanol (163 ps) and water (8 ps), the reflectance measurements of the ethanol-water mixtures [9] can be used as an evaluation of the dynamic range and the sensitivity of the identifiers. The reflectance of the ethanol-water mixtures with varying ethanol content from 0% to 95%, measured by the developed liquid identifier with quasioptical coupling, is presented in fig. 2. The dynamic range of spectral reflectances of 200 has been demonstrated for the scanning times of a few seconds. The best selectivity to ethanol concentration has been achieved at the frequency range 100 - 300 GHz. This selectivity enhancement is related with the second relaxation time τ2 (3 ps) of ethanol [9]. Taking into account the experimental errors, the low concentrations of ethanol in water-ethanol mixtures can be detected with accuracy better than 0.1%.

In conclusion, we have suggested a concept of liquid identification based on Hilbert-transform spectroscopy and high-Tc Josephson detectors. Two demonstrators of liquid identifiers both based on this concept but with various, quasioptical and waveguide, coupling units have been developed.

The frequency bandwidth of 1 – 500 GHz, scanning time of 0.2 - 5 sec and the measurement error of 0.3% has been achieved. The demonstrators have been tested with various pure and impure liquids. The possibility of identification of different types of water, acetone, alcohols, 30% H2O2/H2O, beverages and many other liquids as well as the alcohol concentration in alcohol-water mixtures has been successfully demonstrated.

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